

**ИЗВЕСТИЯ
АКАДЕМИИ НАУК СССР**

**ОТДЕЛЕНИЕ
ХИМИЧЕСКИХ НАУК**

Number 1

January, 1960

BULLETIN OF THE ACADEMY OF SCIENCES OF THE USSR

Division of Chemical Science

(IZVESTIYA AKADEMII NAUK SSSR)

(OTDELENIE KHIMICHESKIKH NAUK)

IN ENGLISH TRANSLATION



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Number 1
January, 1960

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(Otdelenie Khimicheskikh Nauk)

A publication of the Academy of Sciences of the USSR

IN ENGLISH TRANSLATION

Year and issue of first translation:

No. 1

Jan.-Feb. 1952

	<i>U. S. and Canada</i>	<i>Foreign</i>
<i>Annual subscription</i>	<i>\$80.00</i>	<i>\$85.00</i>
<i>Annual subscription for libraries of nonprofit academic institutions</i>	<i>30.00</i>	<i>35.00</i>
<i>Single issue</i>	<i>5.00</i>	<i>5.00</i>

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SOLUBILITY OF SALTS IN AQUEOUS SOLUTIONS OF ELECTROLYTES

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Translated from *Izvestiya Akademii Nauk SSSR, Otdelenie
Khimicheskikh Nauk*, 1960 No. 1, pp 3-8, January, 1960
Original article submitted May 28, 1958

The solubility of salts in aqueous solutions is a complex phenomenon and is the result of many processes occurring in solids and liquids. Here we examine the particular problem of the change in solubility of salts under the effect of a change in the composition and concentration of a solution. Nernst's law explains, mostly qualitatively, the effect of like ions on solubility, e.g., the fall in solubility of silver chloride in the presence of silver ions. However, cases are known where the common ion increases the solubility of the salt. The addition of lead nitrate to a saturated solution of lead chloride first lowers the solubility of the latter but beginning with a concentration of approximately 0.1 mole of lead nitrate per liter of solution, the solubility of lead chloride increases. The effect of unlike ions is expressed even more sharply. At 25°, one liter of water dissolves 2 g of calcium sulfate, but one liter of water containing 3.5 moles of magnesium nitrate dissolves 15 g of calcium sulfate.

According to Lewis [1] the activity is related to concentration:

$$a = \gamma x, \quad (1)$$

where a is the activity, γ the activity coefficient, and x the concentration. The activity may be less or greater than the concentration and consequently, the activity coefficient less or greater than unity. In a saturated solution at constant temperature, the concentration of salts saturating the solution, i.e., in a state of equilibrium with the solid phase, is not constant but depends on the composition and concentration of the solution and on the presence of foreign ions. However, the activity of a saturated solution is constant. The constant value of the activities of a substance in the solid phase or of the same substance in a saturated solution follows from the definition of thermodynamic equilibrium. The equality of these activities requires an additional condition, namely, an identical standard state for the equilibrium phases. In actual fact this condition is not usually obeyed when the equilibrium phases are a solid salt and its aqueous solution. In this case the standard states of the equilibrium phases may not coincide.

The standard state of a solid substance is usually taken as that of the pure solid substance at the experimental conditions or under some given conditions, for example, at 25° and 1 atm. The standard state of a dissolved salt is taken as an infinitely dilute solution, i.e., an ideal solution whose activity equals its concentration and activity coefficient equals unity. This standard state is also adopted in the present work. The inequality of the activity of the solid and the dissolved material in equilibrium with it is of no importance in the problem examined, but the constancy of these values is of very great importance. The numerical values of the activity of the solid salt and the activity of the same salt as a saturated solution are constant at given temperature and pressure and do not depend on the composition and concentration of the solution. The activity is nothing more than ideal solubility and therefore it can be determined from Schröder's equation, but there is another method of determining the activity, namely, from experimental data on the solubility of the salt in water and in two or three dilute solutions

[2,3]. A graphical representation of the relation between solubility and the square root of ionic strength* is used for this purpose. A straight line is usually obtained in such cases and this is readily extrapolated to zero ionic strength where the activity coefficient equals unity and the activity equals the concentration. The activity, which plays such an important role in phenomena occurring in a liquid phase in equilibrium with a solid one, is determined in this way.

Let us examine a system consisting of two phases in a state of equilibrium. One phase is solid and the other a liquid, consisting of a saturated solution of this solid phase and containing an arbitrary amount of dissolved foreign electrolytes. Equation (1) shows that to determine the solubility it is necessary to know the activity coefficient, as the activity is known and remains constant. The Debye-Hückel equation for the activity coefficient is a limiting rule and is accurate for high dilutions only up to ~ 0.01 mole/liter [4]. Nonetheless, this equation is of practical value in all fields of science and technology where the interaction of water or dilute solutions with sparingly soluble salts is examined. An example is the determination of the action of soft natural water on rocks containing calcium carbonate and sulfate. Analysis of the water makes it possible to calculate its ionic strength and by substituting the value of this and also the valence of the ions of the sparingly soluble salt in the Debye-Hückel equation we obtain the activity coefficient of the salt of interest to us and, from Eq. (1), its solubility. The same also applies to the action of water on hydroconstructions of concrete, which contains sparingly soluble salts. Some rare elements, for example thallium and thorium, are now obtained in the form of their sparingly soluble salts from a large volume of electrolyte solutions. The Debye-Hückel equation makes it possible to determine the content of the valuable rare element in solution if it is sufficiently dilute. Naturally, the examples presented do not exhaust all the possible practical applications of the limiting Debye-Hückel law.

The practical value of laws deduced for very dilute solutions continually increases. It is known that completely pure substances do not exist; each substance is a solution, solid or liquid. In considering more concentrated solutions it is necessary to allow for the dimensions of the ions, which are considered as points in the limiting law. A number of papers [4, 5] have been devoted to the problem of the size of ions in solution. One thing is definite: This size is of the same order as the crystallographic diameters of the ions. It can be found empirically if the activity coefficient is known. The Debye-Hückel equation, containing the average effective diameter of the ions, is applicable up to 1 mole/liter in many cases, but due to the indeterminate nature of this value, this equation acquires an empirical character.

Gronwall, La Mer, and Sandved [6] and also Gronwall, La Mer and Greiff [7] subjected the main Debye-Hückel equation to detailed mathematical treatment to allow for the electrical potential close to an ion. These authors obtained more accurate but much more complex equations for the activity coefficient than the first approximation of Debye and Hückel. We applied the Debye-Hückel equation, using the crystallographic dimensions of the ions, but assuming a linear increase in this value with the ionic strength of the solution according to the equation

$$\alpha = \alpha_0 + b \sqrt{\sum m_i z_i^2}. \quad (2)$$

We thus obtained results close to experimental values for complex salt systems up to high concentrations [2, 3].

One of the first attempts at a quantitative examination of concentrated solutions was Hückel's equation [8]. The constant H in this equation must reflect the change in the dielectric constant of the solution with concentration. In actual fact H is an empirical constant and even has a negative value in some cases. If suitable values for the constants α and H are chosen from experimental data, then the Hückel equation may be applied successfully at the highest concentrations [4, 5].

The literature contains a large number of equations for activity coefficients [4, 5, 9-13], all of which are inferior to the equations of Debye and Hückel from a practical point of view; they are cumbersome, contain values which cannot be determined experimentally, and in most cases are only accurate for dilute solutions. In the theories of concentrated solutions developed by Mirskhulava [9, 10], Mikulin [11], Khomutov [12], Falkenhagen [14, 15], Dutta and Bagchi [16, 17], Eigen and Wiche [18], and many other authors allowance is made for the interaction of ions with solvent molecules, which is expressed by introducing the volume of the ions, including

* The ionic strength is $\sum m_i z_i^2$, where m_i is the number of moles of ions of type i per 1000 g of water and z_i is the valence of ions of type i .

their hydration envelope, i.e., the so-called covolume effect. The simplest equation for the activity coefficient of concentrated solutions was proposed by Falkenhagen and Schmutzer [14]:

$$\ln \gamma = - \frac{e^2 z_1 z_2}{2DkT} \frac{x}{1 + \alpha x} - \ln(1 - nv), \quad (3)$$

where n is number of ions in 1 cc of solution and v is the average volume of the ions, expressed in cubic centimeters. This equation is suitable up to 4 moles of 1-1 valent electrolyte per liter of solution. If we have a nonelectrolyte, e.g., a solution of sugar in water, the first term on the right-hand of the equation, which coincides with the Debye-Hückel equation, drops out as the solution contains no ions, whose electrostatic interaction is reflected by this term. In this case the activity coefficient depends only on the interaction between nonelectrolyte molecules and solvent molecules, i.e., is determined by one covolume effect:

$$\gamma = \frac{1}{1 - nv} \quad (4)$$

Equation (4) is applicable to solutions of sugar in water with concentrations up to 1.5 moles/liter and shows that the activity coefficient of sugar is greater than unity even in the most dilute solutions; n is the number of molecules of dissolved substance in 1 cc of solution, i.e., a value of the order of 10^{20} , and v is the volume of one sugar molecule, a value of the order of 10^{-24} as the linear dimensions of the molecule are of the order of 10^{-8} cm. Consequently, the product nv is a small fraction so that the denominator is less than unity and γ is greater than unity. The equation of Falkenhagen and Schmutzer contains two empirical constants, α and v , which are not related to each other. In this respect, Eq. (3) is similar to Hückel's equation.

Our problem was to study solubility in complex salt systems. The desire to avoid empirical constants and the impossibility of applying Debye and Hückel's theoretical equation to our systems, which consisted of concentrated solutions, compelled us to reject existing equations for the activity coefficient and to search for a new method. We considered the solubility x as the product of two factors, namely, the solubility coefficient β and the activity:

$$x = \beta a. \quad (5)$$

The activity is a constant value. The solubility isotherms of salts in aqueous electrolyte solutions have various forms, namely, curves rising or falling with concentration and passing through a maximum or a minimum. Here we examine the problem of a deviation of the solubility from a straight line parallel to the concentration axis at constant temperature. In determining the solubility coefficient, we started from the simplest premises. We assumed that the solubility coefficient increases with the electrostatic interaction of the ions and falls with a decrease in the volume concentration of water:

$$\beta = \frac{z_1 z_2 \dots \sqrt{\sum m_i z_i^2}}{\frac{D_1 - D}{C}}. \quad (6)$$

The numerator expresses the electrostatic interaction of the ions and z_1 and z_2 are the valences of the solid ions, while the ionic strength of the solution is under the square root sign. The denominator represents the fall in volume concentration of water per mole of dissolved substance; D_1 is the number of moles of water in 1 liter of pure water and at 25° $D_1 = 55.3434$, while D is the number of moles of water in 1 liter of solution:

$$D = \frac{55.506 d}{1000 + g}, \quad (7)$$

where 55.506 is the number of moles of water in 1000 g of water, d is the solution density, g is the total number of grams of dissolved substances per 1000 g of water, and C is the total number of moles of all dissolved substances in 1 liter of solution, i.e., $C = \sum c_i$, where c_i is the number of moles of substance i per liter of solution:

$$c_i = \frac{1000 m_i d}{1000 + g}, \quad (8)$$

where m_i is the number of moles of substance i per 1000 g of water.

Equation (6) explains the course of the solubility isotherms and for systems consisting of sparingly and readily soluble salts, it may even be used to predict the solubility. In the latter case the concentration or solubility of the sparingly soluble salt is so small in comparison with the total concentration that it can be neglected in calculating the ionic strength. In this case the density of the solution is changed only insignificantly as a result of the presence of ions of the sparingly soluble salt. Therefore, the solubility coefficient of the sparingly soluble salt can be determined from Eq. (6) if the concentration and density of the solution of readily soluble salts are known. Equation (6) is also applicable to cases where the solubility isotherm has a maximum, for example, the solubility of calcium sulfate and carbonate in aqueous solutions of sodium chloride [19]. Here the ionic strength and the fall in volume concentration of water per mole of dissolved substance, i.e., the numerator and denominator of Eq. (6), increase with concentration but at different rates and as a result the solubility coefficient β passes through a maximum. Since the activity is constant, then according to Eq. (5) the solubility also has a maximum. The constancy of the activity is a criterion not only of equilibrium, but also of the absence of reaction in the liquid phase. Solution of carbonate in water containing CO_2 is accompanied by the formation of bicarbonate. In this case the activity obeys the law of mass action [3, 19, 20].

Equation (6) was checked for complex salt systems containing 1-1, 2-2, and 2-1 valent electrolytes up to three moles of dissolved salts per 1000 g of water under conditions of accurately determined density from unity in the fifth place of decimals to unity in the fourth place in relation to solution concentration. For the most dilute solutions it was necessary to determine the density with an accuracy up to the sixth place. As an example, let us determine the solubility of calcium sulfate in aqueous solutions of sodium chloride and calcium bicarbonate at 25°. Let us take a solution containing 1.012 mole of sodium chloride and 0.0060 mole of calcium bicarbonate per 1000 g of water. The activity of calcium sulfate in saturated solutions of this salt at 25° equals 0.00641 [2, 19, 20]. The solubility coefficient of calcium sulfate:

$$\beta = 4 \sqrt{\sum m_i z_i^2} \frac{C}{D_1 - D}, \quad (9)$$

and the ionic strength of the solution $\sum m_i z_i^2 = 1.012 \cdot 2 + 0.0060 \cdot 6 = 2.060$.

The interpolated value of the solution density $d = 1.0443$ g/cc. According to Formula (8) $C_{\text{NaCl}} = 0.9969$; $C_{\text{Ca}(\text{HCO}_3)_2} = 0.0059$, and hence $C = C_{\text{NaCl}} + C_{\text{Ca}(\text{HCO}_3)_2} = 1.0028$.

From Formula (7), $D = 54.6772$. By substituting the values found in Eq. (9) we obtain: $\beta = 8.639$ and hence the solubility of calcium sulfate $x = \beta a = 0.055$.

The experimental value of $x = 0.047$ mole per 1000 g of water [20]. If we consider the calcium sulfate, then we obtain: 0.047 mole of $\text{CaSO}_4 = 6.399$ g. In 1000 g of water there will be 66.527 g of dissolved salts and hence $C_{\text{NaCl}} = 0.9909$; $C_{\text{CaSO}_4} = 0.0460$; $C_{\text{Ca}(\text{HCO}_3)_2} = 0.0059$; $C_{\text{NaCl}} + C_{\text{CaSO}_4} + C_{\text{Ca}(\text{HCO}_3)_2} = 1.0428$; $D = 54.3491$; $D_1 - D = 0.9943$; $\sum m_i z_i^2 = 2.436$; $\beta = 6.550$ and $x = \beta a = 0.042$.

This result is close to the experimental value, but the first value (0.055) is more important to us as in it we see not only the explanation of the phenomenon, but also the prediction of it.

The density of the solution was obtained by interpolation, which is the main reason for the discrepancy between the results obtained and experimental data.

SUMMARY

1. A method is proposed for determining solubility, in which the latter is considered as the product of the solubility coefficient and the activity.
2. According to the equation deduced, the solubility coefficient depends on the electrostatic interaction of the ions and the volume concentration of water.
3. Calculated data were confirmed by experimental solubility isotherms of salts in aqueous solutions of electrolytes.

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ADSORPTION OF WATER VAPOR ON IONIC CRYSTALS

COMMUNICATION 2. NONEQUILIBRIUM SORPTION OF WATER ON LEAD IODIDE CRYSTALS

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Translated from *Izvestiya Akademii Nauk SSSR, Otdelenie
Khimicheskikh Nauk* 1960, No. 1, pp. 9-14, January, 1960
Original article submitted April 23, 1958

In the first communication [1], we examined the results, as well as procedures, of investigating the adsorption of water vapor on crystalline powders of AgI and AgCl. We also discussed the relation between the parameters of the AgI and PbI_2 crystal lattices, which are analogous to the ice lattice, and the capacity of these particles to serve as crystallization nuclei in a supercooled cloud. In the work [1], the adsorption of water on AgI and AgCl had a van der Waals character without any complications of the sorption process either at positive or negative temperatures. At the same time, cases are described in the literature where the physical adsorption of water on ionic crystals is sometimes so peculiar that in this connection it may be compared with chemisorption [2-5]. In this connection, the adsorption of water vapor on PbI_2 crystals is a very characteristic example. The sorption of water vapor on AgI and AgCl crystals, which we examined in communication 1, differs essentially from the sorption of water on PbI_2 crystals. While in the first case we were dealing with practically rapid, reversible, purely physical adsorption, in the second case we were dealing with a complex process, which was very protracted.

EXPERIMENTAL

A preliminary investigation of the sorption isotherms for water vapor on PbI_2 at 20° showed that sorption equilibrium was not established for a long time. Systematic absorption of water vapor by the adsorbent was observed for several hours after the admission of a portion of water vapor. Special investigations were made to elucidate the kinetics of the process and the results are presented graphically in Fig. 1. Each curve in Fig. 1, represents an independent series of measurements of the kinetics of water vapor sorption at 20° on PbI_2 crystals. Before the beginning of each series of measurements, the adsorbent was heated in vacuum at $110-120^\circ$ for 5 hours. As Fig. 1 shows, the greatest increase in weight of the adsorbent occurred over the first 3-10 min from the moment of admission of vapor into the system. The rate of water absorption by the adsorbent subsequently decreased but nonetheless remained appreciable and equilibrium was not reached after 2 hr.

A different type of sorption kinetics was observed at -20° (Fig. 2). The curves on this graph indicate that the greatest increase in weight of the adsorbent occurred in the first 3-5 min and then the sorption rate decreased strongly, and after only 60-80 min after the admission of water vapor into the system hardly any change in sorption was observed. As in the previous graph, each curve on this graph represents an independent series of measurements on a preliminarily heated adsorbent. In Fig. 2 the upper curve corresponds to sorption kinetics at a relative pressure of 0.79. In the calculations in this case the value of p_s was taken as equal to the saturated vapor pressure over water supercooled to -20° . The maximum possible value of p/p_s equaled 0.8, as in our apparatus at -20° it was impossible to obtain a pressure above 0.77 mm Hg since the excess vapor immediately condensed as ice on the walls of the balance case. Prolonged experiments at 19° and a water vapor pressure of 1.7 mm showed that even after 35 days sorption equilibrium was not attained in the system.

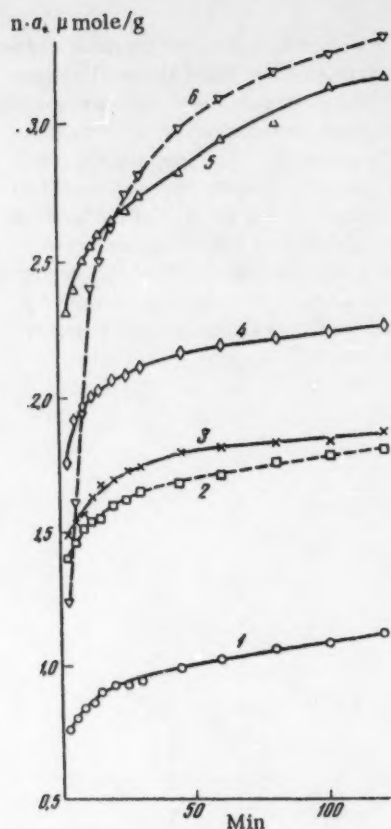


Fig. 1. Kinetics of water vapor sorption on lead iodide at 20° (n is the scale coefficient on the ordinate axis): 1) $n=1$, $p/p_s = 0.04$; 2) $n=2$, $p/p_s = 0.56$; 3) $n=1$, $p/p_s = 0.18$; 4) $n=2$, $p/p_s = 0.76$; 5) $n=1$, $p/p_s = 0.38$; 6) $n=10$; $p/p_s = 0.95$.

of the sorption process as a whole. The hydration process, which must involve chemical forces, is characterized by an activation energy. This explains the considerable effect of temperature on the sorption kinetics (Figs. 1 and 2). In particular, the slow component of the sorption process becomes practically imperceptible at a low temperature.

Naturally, the efficiency of PbI_2 particles in their nucleation of a supercooled cloud appears over a short time interval (tens of minutes). Therefore, despite the fact that in the sorption of water vapor on PbI_2 , sorption equilibrium was not attained even after several tens of days, we considered it profitable to investigate this process. However, in order to measure the water vapor sorption isotherm at positive temperatures over a practically convenient time, it was necessary to choose some arbitrary state of the system, naturally, nonequilibrium, which would correspond to a definite amount of sorption. Therefore, as the reading of the amount of sorption we took the value corresponding to the amount of sorption after 2 hours from the admission of each portion of vapor.

The nonequilibrium sorption isotherms measured for water vapor on PbI_2 at 20, 10, and 0° are given in Fig. 3. The broken curves refer to adsorbent which was heated in vacuum before the measurements; the solid curves refer to a sample which first sorbed water and was then evacuated at room temperature. The graphs show the results of three or four independent series of measurements. It should be noted that we did not introduce a correction into the measured isotherms for the amount of water vapor adsorption by the glass dish, as the measurements were made in a nonequilibrium vapor-adsorbent system. Even in this case the amount of adsorption on lead iodide was

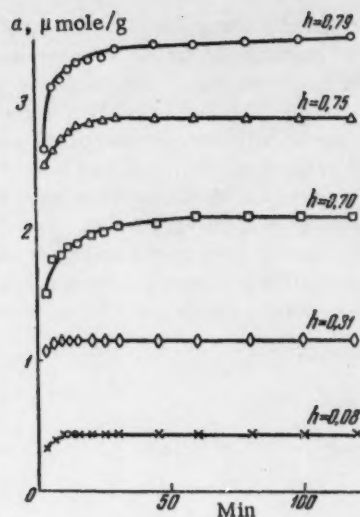


Fig. 2. Kinetics of water vapor sorption on lead iodide at -20° ($h = p/p_s$ is the relative pressure).

The slow course of the sorption of water vapor on PbI_2 was apparently caused by the fact that on top of the physical adsorption process is superposed some other process which is very protracted. A comparison of the curves in Figs. 1 and 2 shows that the kinetics of the water sorption process depend on the experimental temperature. In our opinion, one of the processes complicating the van der Waals sorption of water on PbI_2 may be a hydration process, which, in general, can occur both on the surface and in the volume of the adsorbent. However, it is apparently impossible to determine the fraction of the total amount of sorption which pertains to each of these processes. If hydration (surface and volume) actually occurs, then it is precisely its rate which will determine the kinetics

considerably greater than the adsorption of water on the dish. Thus, for example, at positive temperatures and over wide range of relative pressures the amount of adsorption on the dish was not more than 12% of the total amount of sorption measured, i.e., somewhat exceeded the experimental error. All the isotherms are of type II according to Brunauer's classification. The isotherms examined were characterized by noncoincident branches for sorption and desorption, i.e., the peculiar phenomenon of hysteresis. Reproducibility of the hysteresis loop was observed only after the adsorbent had been kept for 35-40 hours in an atmosphere saturated with water vapor at room temperature. Naturally the hysteresis phenomenon was caused by the kinetics of the process, but the size of the loop was determined by the total time of the experiment. By increasing the time at any point on the desorption curve (above 2 hours) it was possible to cause the desorption branch to approach the sorption branch. Thus, for example, after 6 hours at the desorption point on the isotherm at $p/p_s = 0.2$ and 20° , the amount of adsorption changed by $0.5 \mu\text{mole/g}$. After prolonged pumping out at the experimental temperature, the amount of residual sorption,

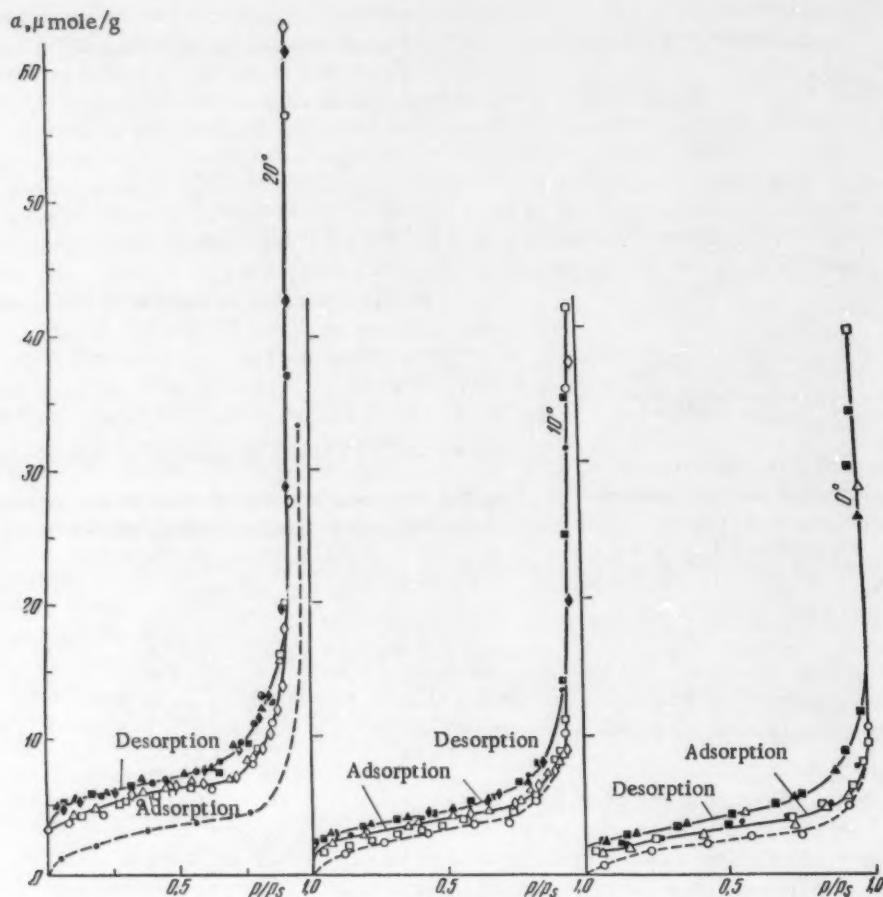


Fig. 3. Sorption isotherms for water vapor on lead iodide at 20, 10, and 0° .

i.e., the amount of water which was irreversibly held by the lead iodide sample, was approximately $3 \mu\text{mole/g}$ for the isotherm at 20° . The amount of residual sorption for the isotherms at 10 and 0° was less and equaled $1.8-2 \mu\text{mole/g}$.

It was impossible to calculate the size of the specific surface of the adsorbent from the experimental water vapor sorption isotherms for PbI_2 as equilibrium was not attained in the system. On the other hand, as the surface of the PbI_2 powder was small, the accuracy of measuring the adsorption isotherm for nitrogen at its boiling point, without radical alteration of the apparatus, would be inadequate (convection currents and small amounts of adsorption).

In addition to this there were experimental difficulties connected with the unsealing of the ground joint of the sorption tube. We therefore calculated the specific surface of the crystalline powder of PbI_2 from the benzene vapor adsorption isotherms by the method of Brunauer, Emmett, and Teller (BET). According to the data of various authors [6-8], the area occupied by a benzene molecule in condensed monomolecular layer, ω_0 , varies from 32.2 to 51.8 \AA^2 , depending on the properties of the adsorbent surface. For the adsorbent studied it was difficult to make a choice in favor of any of these values of ω_0 . In our calculations the actual value of ω_0 for a benzene molecule was determined by an indirect method. The specific surface of the finely dispersed PbI_2 powder (prepared by sublimation) was first calculated from the nitrogen adsorption isotherms at the boiling point of nitrogen, which were measured on another apparatus by a gravimetric method (ω_0 for a nitrogen molecule equals 16.2 \AA^2 [10]). Then, knowing the value of the specific surface by the nitrogen method, we used the benzene adsorption isotherm to calculate ω_0 for the C_6H_6 molecule and this was found to equal 50 \AA^2 .

The measured isotherm for benzene adsorption on a spectrally pure sample of PbI_2 was completely reversible over the whole range of relative pressures studied and was well described by the linear form of the BET equation. The calculated specific surface S for PbI_2 powder equaled 0.25 m^2/g . We then calculated the volume of a monomolecular layer a_m , assuming as previously [1], that for a water molecule $\omega_0 = 26 \text{\AA}^2$, and obtained the value $a_m = 1.6 \text{ }\mu\text{mole/g}$. It should be noted that the amount of residual sorption in general was close to the value of a_m found. This agreement makes it possible to assume with some reliability that at positive temperatures the surface of PbI_2 is apparently covered with a statistical monomolecular layer of water.

We note that a change in temperature of 20° (from 20 to 0°) had no essential effect on the form and character of the isotherm, though the amount of residual sorption decreased somewhat with a fall in the experimental temperature. The recorded value of the amount of water vapor sorption at positive temperatures (including 0°) was largely due to hydration of the adsorbent and therefore an increase in the time interval over which the sorption curves of the isotherms were plotted involved an increase in the total sorption. For example, at 20° and $p/p_s = 0.85$, 2 hours after the admission of the portion of water vapor the amount of sorption was $\sim 30 \text{ }\mu\text{mole/g}$, but after 6 hours it equaled $\sim 60 \text{ }\mu\text{mole/g}$. If it is assumed that the actual process of water vapor sorption on PbI_2 , as a provisional process, is caused by physical phenomena, then 60 $\mu\text{mole/g}$ of water is sufficient to cover the adsorbent surface with 35-37 statistical monomolecular layers. On the other hand, according to data in [11], under the same conditions 125 monomolecular layers of water are obtained, i.e., four times greater and the author considered the water vapor sorption process as a purely physical process.

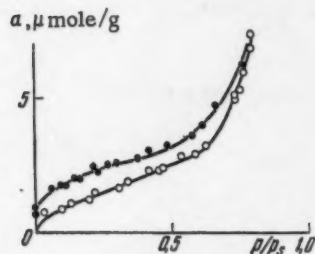


Fig. 4. Sorption isotherm for water vapor on lead iodide at -20° .

The sorption isotherm for water vapor on PbI_2 at -20° (Fig. 4) shows that at this temperature also the sorption process proceeds supposedly according to the mechanism described above. The difference consists of the fact that actual equilibrium is attained after 60-80 min. Again, if the sorption of water in this case is considered as some hypothetical process of physical adsorption, then according to calculations the first layer is filled at $p/p_s = 0.25$ and the amount of limiting sorption is $\sim 8 \text{ }\mu\text{mole/g}$, i.e., five monomolecular layers. The amount of residual sorption is considerably less than at positive temperature and is $\sim 0.8 \text{ }\mu\text{mole/g}$.

We consider that it can be supposed with a certain degree of probability that water adsorbed on PbI_2 at -20° is present as a supercooled liquid. Since our own experimental data do not make it possible to assess reliably the accuracy of this hypothesis, we turned to work [12-16] in which the authors clearly showed that in the adsorption of various vapors (including water) on solids at temperatures considerably below the triple point, the adsorbed substance was in the form of a supercooled liquid. If this is actually the case, then in our investigations it is necessary to take the value of p_s as the saturated vapor pressure over supercooled water at the experimental temperature in calculating the relative pressures. In Fig. 4, p/p_s is plotted for supercooled water.

In conclusion it should be noted that on the basis of our experiments we were unable to establish a relation between the adsorption behavior of lead iodide and the capacity of particles of it in an aerosol to act as crystallization nuclei in the nucleation of supercooled clouds. In all probability these properties of PbI_2 particles appear in the temperature region that we did not investigate. Apart from this, it is extremely possible that defects and

imperfections in the crystallites of a PbI_2 aerosol play an important part in artificial rain-making. All these problems undoubtedly require special investigations that are beyond the limits of the present work.

The authors would like to thank B.P. Bering, V. V. Serpinski, and A. V. Kiselev for valuable comments and interest in this work and also I. I. Angelov for assistance in preparing spectrally pure adsorbents.

SUMMARY

1. Nonequilibrium sorption isotherms for water vapor on lead iodide crystals with a specific surface of $\sim 0.2 \text{ m}^2/\text{g}$ over the temperature range from 20 to -20° were investigated.
2. Over the whole pressure range investigated, the sorption isotherms were irreversible. The process of water vapor sorption on PbI_2 is very protracted, especially at positive temperatures; equilibrium was not attained at 20° even after 35 days.
3. The investigation showed no relation between the adsorption behavior of lead iodide and the capacity of its particles as an aerosol to act as crystallization nuclei in the artificial nucleation of supercooled clouds.

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* Original Russian pagination. See C. B. Translation.

KINETICS OF 2-VINYLPYRIDINE HYDROGENATION ON A RANEY NICKEL CATALYST

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Translated from *Izvestiya Akademii Nauk SSSR, Otdeleniye Khimicheskikh Nauk* 1960.

No. 1, pp 15-20, January, 1960

Original article submitted April 25, 1958

Original article submitted April 25, 1958

Hydrogenation of the ethylene bond in vinylpyridine has been little studied previously. In some work [1, 2], vinylpyridine was hydrogenated either for preparative purposes or to demonstrate its structure. Likewise, the kinetics of vinylpyridine hydrogenation have not been investigated.

In the work of Nikitskaya and Rubtsov [3], the hydrogenation of 4- (β , β -dicarboethoxy)-vinylpyridine in the presence of a Raney nickel catalyst was investigated. It was established that various compounds were formed, depending on the reaction conditions: Only the side double bond was hydrogenated at 80-100°; 1,4-di-(pyridyl-4)-2,2,3,3-tetracarboethoxybutane was formed in addition to hydrogenation of the double bond at 20°; while at 140-160° in ethyl alcohol and also in methyl alcohol and dioxane, the pyridine nucleus was hydrogenated and there was simultaneous decarboethoxylation and alkylation at the nitrogen.

In the present work we present experimental material from a study of the kinetics of 2-vinylpyridine hydrogenation on a Raney nickel catalyst over the temperature range from 5 to 40°. In addition, it seemed interesting to compare the hydrogenation of 2-vinylpyridine and styrene. As the kinetics of styrene hydrogenation have been studied quite thoroughly by other authors, in the present work we only carried out a few experiments to study the effect of styrene concentration on the reaction rate under conditions analogous to those for the hydrogenation of 2-vinylpyridine.

EXPERIMENTAL

The hydrogenation was carried out in a thermostatted glass hydrogenation vessel, 180 mm long and 30 mm in diameter, on a fast rocker with a travel of 12.7 cm. Freshly prepared 2-vinylpyridine, obtained by dehydration of 2-(β -hydroxyethyl)-pyridine, was used in the experiments. The product had the following constants, which agree completely with literature data: b.p. 55° (15 mm); n_D^{20} 1.5500; d_4^{20} 0.9758. The catalyst was prepared by extracting a 50% NiAl alloy with 20% NaOH at 100° for 2 hours. A fresh portion of catalyst (0.54 g as a paste) was used in each experiment. Freshly distilled 96% ethyl alcohol was used as solvent. Electrolytic hydrogen, freed from oxygen, was used for hydrogenation.

The Raney nickel catalyst paste was taken with a special spoon and washed from it with 10 ml of alcohol into a hydrogen-flushed hydrogenation vessel. The alcohol was decanted and the catalyst washed twice with alcohol (10-ml portions). To the catalyst in the hydrogenation vessel was added 10 ml of alcohol and then it was saturated with hydrogen for 20 min under the same conditions (temperature and mixing rate) as for the hydrogenation. The solvent was removed by filtration and a sample of 2-vinylpyridine, dissolved in 10 ml of 96% ethyl alcohol, introduced. All operations (introduction and washing of catalyst, decantation, filtration, introduction of substance for hydrogenation, etc) were carried out in a hydrogen atmosphere.

TABLE 1

Effect of Mixing Rate on the Rate of 2-Vinylpyridine (0.3986 g) Hydrogenation

Expt. No.	Number of shakes per min	Average rate up to the absorption of $1/2 v_0$ of H_2 in ml/0.5 min	Half-reaction time in min
1	230	5.6	3.4
2	360	6.5	2.8
3	500	8.1	2.2
4	650	7.9	2.2
5	900	8.0	2.1

TABLE 2

Effect of Amount of Catalyst on the Rate of 2-Vinylpyridine (0.5974 g) Hydrogenation

Expt. No.	Catalyst weight in g	Average rate up to the absorption of $1/2 v_0$ of H_2 in ml/0.5 min	Half-reaction time in min
6	0.54	9.9	3.2
7	1.05	18.2	1.7
8	1.55	25.1	1.2
9	2.00	32.4	0.9

We determined the extent of hydrogenation from the volume of hydrogen consumed, and the rate of hydrogenation and the activity of the catalyst from the rate of hydrogen absorption with time. The results obtained are presented in the form of kinetic curves of the reaction rate $\frac{\Delta v_0}{\Delta t}$ against the total volume of hydrogen absorbed $\frac{\Sigma \Delta v_0}{2}$. The volumes of hydrogen absorbed on the curves and in the tables have been corrected to normal conditions.

Results of measurements. We first studied the conditions under which the reaction proceeded in the kinetic region. The results obtained (Table 1) show that with an increase in the mixing rate from 230 to 500 shakes per min, the rate of 2-vinylpyridine hydrogenation in ethyl alcohol increased. Beginning with 500 shakes per min, the rate of hydrogen absorption remained practically constant. The latter characterizes transition into the kinetic region [4]. All subsequent experiments were carried out with vigorous mixing (900 shakes per min).

TABLE 3

Effect of 2-Vinylpyridine Concentration on Reaction Rate

Expt. No.	Weight of 2-vinylpyridine in g	Average rate up to the absorption of $1/2 v_0$ of H_2 in ml/0.5 min	Half-reaction time in min
10	0.3987	9.0	2.3
11	0.7976	9.0	4.4
12	1.1949	8.6	7.2

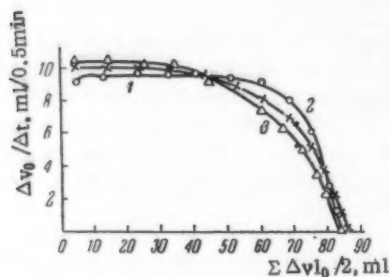


Fig. 2. Effect of reaction products on the rate of 2-vinylpyridine hydrogenation: 1) Without products added; 2) during second hydrogenation; 3) with 2 ml of 2-ethylpyridine added.

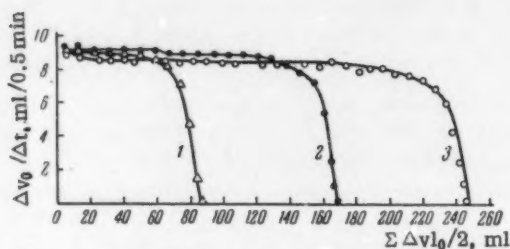


Fig. 1. Effect of 2-vinylpyridine concentration on reaction rate: 1) 0.3987; 2) 0.7976; 3) 1.1949 g.

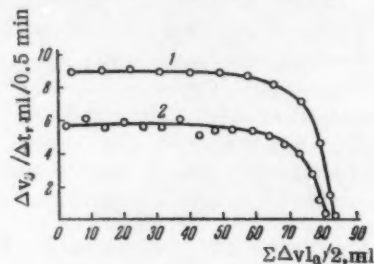


Fig. 3. Effect of solvent on 2-vinylpyridine hydrogenation: 1) in 96% C_2H_5OH ; 2) in C_6H_6 .

Table 2 gives data on the effect of the amount of catalyst on the rate of 2-vinylpyridine hydrogenation. This table shows that at a constant mixing rate the reaction rate increases in direct proportion to the increase in the amount of catalyst. This relation between reaction rate and the amount of catalyst is characteristic of the kinetic region.

We then studied the order of the reaction of 2-vinylpyridine hydrogenation. The results obtained are given in Table 3. Figure 1 gives curves illustrating the results of these experiments. Curves 1-3 show that the hydrogenation of 2-vinylpyridine is a zero order reaction with respect to the compound hydrogenated. The hydrogenation rate remained constant up to the absorption of 50% of the theoretically required amount of hydrogen. The observed zero order of the reaction was also confirmed in experiments on the hydrogenation of 2-vinylpyridine at various concentrations (Fig. 1, curves 1-3). Thus, with a change in the vinylpyridine concentration by a factor of three, the reaction rate did not change (Table 3, cf. experiments 10 and 12), while the half-reaction time increased by a factor of three. When a fresh sample of 2-vinylpyridine was hydrogenated on the same portion of catalyst, the reaction rate remained almost constant (Fig. 2, curves 1 and 2). Thus, the catalyst was not deactivated during the reaction. The reaction products also had no retarding action on the reaction. Thus, when 2 ml of 2-ethylpyridine was added to a sample of 2-vinylpyridine in 10 ml of 96% ethyl alcohol, the reaction rate did not change (Fig. 2, curve 3) and the theoretical amount of hydrogen was absorbed.

TABLE 4

Hydrogenation of 2-Vinylpyridine at Various Temperatures

Expt. No.	Weight of substance in g	Hydrogen consumption in ml		Experimental temperature		Hydrogen absorption rate in ml/0.5 min	lg K
		theoret	actual	°C	$\frac{1}{T} \cdot 10^{-3}$		
13	0,8364	178,4	180,3	5,4	359,0	5,2	0,7160
14	0,7974	170,2	168,5	10	353,1	6,2	0,7924
15	0,7974	170,2	166,2	15	346,9	7,5	0,8751
16	0,7976	170,2	162,6	20	341,0	8,8	0,9445
17	0,8364	178,4	181,4	25	335,4	10,2	1,0086
18	0,7976	170,2	166,9	30	329,9	12,2	1,0864
19	0,7976	170,2	165,8	35	324,4	13,9	1,1430
20	0,7976	170,2	168,0	40	319,2	14,8	1,1703

TABLE 5

Hydrogenation of Styrene

Expt. No.	Weight of styrene in g	Av. rate up to adsorption of $1/2 v_0$ of H_2 , ml/0.5 min	Half reaction time in min	Expt. No.	Weight of styrene in g	Av. rate up to adsorption of $1/2 v_0$ of H_2 , ml/0.5 min	Half reaction time in min
21	0,3875	11,4	3,3	24	0,4135	12,5	3,2
22	0,3875	11,65	3,2	25	0,4135	11,4	3,4
23	0,7750	11,1	7,1	26	0,4135	10,4	4,0

It was previously shown [5] that treatment of Raney nickel catalyst with pyridine sharply reduced its activity in hydrogenation of the triple bond in toluene and the conjugated double bond in cyclopentadiene. Hydrogenation of the isolated bond $C=C$ did not occur in this case. The absence of a self-poisoning effect in the hydrogenation of 2-vinylpyridine on the same catalyst is very interesting and it might be explained in the following way. The olefin bond in such a system has a high reactivity. A molecule adsorbed on the catalyst surface is apparently mainly oriented with its double bond towards the catalyst. This is also confirmed by previously published results on the hydrogenation of styrene [6] and also by experiments in our laboratory on the simultaneous hydrogenation of 2-vinylpyridine or cinnamaldehyde in a mixture with cyclopentadiene. Here both cinnamaldehyde and 2-vinylpyridine were hydrogenated simultaneously with the conjugated double bond of cyclopentadiene.

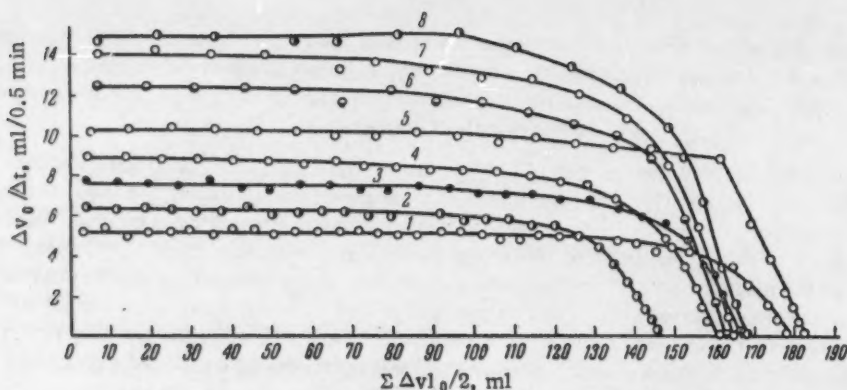


Fig. 4. Kinetic curves of 2-vinylpyridine hydrogenation at various experimental temperatures: 1) 5.4°; 2) 10°; 3) 15°; 4) 20°; 5) 25°; 6) 30°; 7) 35°; 8) 40°.

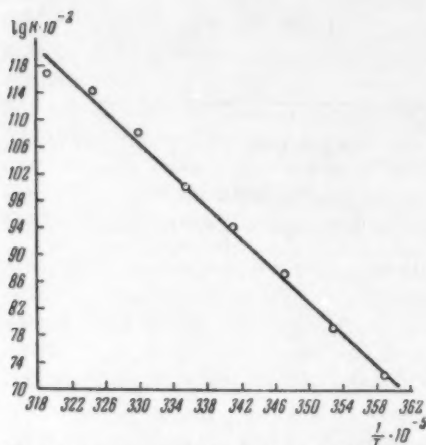


Fig. 5. Temperature dependence of the logarithm of the rate constant.

The reaction remained zero order when 2-vinylpyridine was hydrogenated in benzene (Fig. 3, curve 2). However, the reaction rate in this case was a factor of 1.6 less than in 96% ethyl alcohol. In these experiments, after being washed with alcohol, the catalyst was further washed with benzene (three times with 10 ml portions) and then saturated with hydrogen in 10 ml of benzene.

The temperature coefficient of the reaction was determined in the next experiments. The kinetic curves and the results of these experiments are shown in Fig. 4 and Table 4. As can be seen, with a rise in temperature from 5 to 40°, the hydrogenation rate increased by a factor of approximately three, but the reaction remained zero order with respect to the substance hydrogenated. As the process is zero order, the rate of hydrogen absorption can serve as the reaction rate constant. The true activation energy over the temperature range 5-40° calculated from these data (Fig. 5) equaled 5.6 kcal/mole.

An equimolecular amount of styrene was used for the hydrogenation of styrene in 96% ethyl alcohol under analogous conditions (25° and 0.54 g of Ni as paste). The mixing rate was 900 shakes per min. The results obtained are presented in Table 5 and Fig. 6. Figure 6 shows that the hydrogenation of styrene was also a zero order reaction and this agrees with literature data [7]. The reaction rate remained constant up to the absorption of almost 60% of the theoretically required amount of hydrogen. When a fresh sample of twice the amount of styrene was hydrogenated on the same portion of catalyst, the reaction rate hardly changed (Fig. 6, curves 1-3).

A comparison of the data in Table 3 with those in Table 5, and of Figs. 1 and 2 with Fig. 6 shows that the hydrogenation rates of 2-vinylpyridine (9.0 ml/0.5 min) and styrene (11.5 ml/0.5 min) were similar, though the latter was slightly greater.

SUMMARY

1. The kinetics of 2-vinylpyridine hydrogenation in the presence of Raney nickel catalyst over the temperature range 5-40° and at normal pressure were investigated.
2. The hydrogenation of 2-vinylpyridine in 96% ethyl alcohol proceeds at a high rate; in benzene solution the reaction rate was a factor of approximately 1.6 less. With a rise in temperature from 5 to 40°, the reaction rate increased by a factor of approximately three. Over the given temperature range the reaction was zero order. The true activation energy equaled 5.6 kcal/mole.

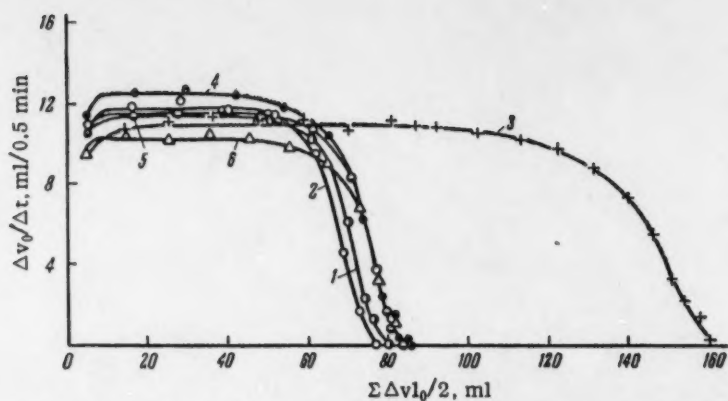


Fig. 6. Hydrogenation of styrene: 1) 0.3875 g (experiment 21); 2) 0.3875 g (experiment 22); 3) 0.7750 g (experiment 23); 4) 0.4135 g (experiment 24); 5) 0.4135 g (experiment 25); 6) 0.4135 g (experiment 26 on another sample of catalyst).

3. The hydrogenation of styrene under analogous conditions was also a zero order reaction, like the hydrogenation of 2-vinylpyridine. Replacement of one of the hydrogens of ethylene by an α -pyridyl radical had almost the same effect on the rate of hydrogenation over Raney nickel as replacement by a phenyl radical.

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*Original Russian pagination. See C. B. Translation.

RELATION BETWEEN THE MACROSTRUCTURE
OF ALUMINUM OXIDE AND THE ACTIVITY OF
NICKEL-ALUMINA CATALYSTS WITH
VARIOUS NICKEL CONTENTS

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Translated from *Izvestiya Akademii Nauk SSSR,*
Otdelenie Khimicheskikh Nauk 1960, No. 1,
pp. 21-23, January, 1960

Original article submitted May 5, 1958

The relation of the activity and stability of catalysts to the amount of nickel deposited has been the subject of a series of investigations. Shuikin and his co-workers found that deposited nickel-alumina catalysts containing 20 and 30% nickel had the same activity in the dehydrogenation of cyclohexane [1]. Catalysts prepared by deposition of 2 and 4% nickel on birchwood charcoal had low activity and low stability in the dehydrogenation of cyclohexane [2]. Similar results were obtained by Novikov and his co-workers for catalysts obtained by decomposition of nickel formate, deposited on activated charcoal or aluminum oxide [3]. However, the possible effect of the macrostructure of the carrier was not studied in this work.

We previously established [4] that the activity of deposited nickel-alumina catalysts in the dehydrogenation of cyclohexane is largely determined by the nature of the porosity of the carrier, i.e., aluminum oxide, and not by the size of its specific surface. Catalysts on coarsely porous aluminum oxide had high activity and stability, while those on finely porous alumina had a low activity regardless of the size of the specific surface. Nickel deposited in the pores of the carrier filled them and made them less accessible. Therefore, it was to be expected that the activity and stability of nickel-alumina catalysts with various nickel contents would also depend on the nature of the macrostructure of the carrier. Nickel-alumina catalysts on three different samples of aluminum oxide were prepared in order to determine this relation.

Coarsely porous samples 1 and 2 were prepared by firing at 500° commercial aluminum hydroxide that had been treated with steam under various conditions [5]. Finely porous sample 3 was prepared by precipitation with ammonia from aluminum nitrate solution at 20°. The specific surface of the catalysts was determined in a high-vacuum apparatus with MacBain quartz spring balances [6]. Adsorption isotherms for benzene at 0° were obtained. The surface was calculated by the BET method [7] with the assumption that the benzene molecule occupies an area of 46.5 \AA^2 [8].

All the aluminum oxide samples were first fired at 500° for 4 hours, then impregnated with 0.5 M nickel nitrate solution with slow evaporation, fired for 4 hours at 400° to decompose the nitrate, and formed into grains $4 \times 2 \text{ mm}$ in size. In this way, catalysts containing 2, 5, 10, 30, and 50 weight % nickel were prepared from each of the aluminum oxide samples. Reduction was carried out at 350° with electrolytic hydrogen, carefully freed from oxygen, moisture and other impurities. The activity of the catalyst was characterized by the degree of

dehydrogenation of cyclohexane, determined refractometrically [9]. The dehydrogenation was carried out in a stream of hydrogen at 300° and a space velocity of 0.3 hr⁻¹. The composition of the gases liberated was determined with a VTI apparatus.

The table gives data on the change in the character of the macrostructure of the samples after deposition of nickel on them. Sample 1 of aluminum oxide had the widest pores with a range of pore radii from 20 to 100 Å. The maximum on the pore radius distribution corresponded to 65 Å. When 5% of nickel was deposited, the radius at the maximum on the pore radius distribution decreased (56 Å), probably due to coating of the inside pore surface by nickel. The degree of cyclohexane dehydrogenation on this catalyst was 59.4% (experiment 1). It was to be expected that when 10% of nickel was deposited, then the degree of covering of the surface would be increased. A further displacement of the maximum on the pore radius distribution towards narrower pores was observed. The total pore volume, characterized by the amount of benzene absorbed at saturation, also decreased. The activity of the catalyst was higher and the degree of cyclohexane dehydrogenation was 89% (experiment 2). The relation examined was investigated in more detail on catalysts prepared by deposition of various amounts of nickel on aluminum oxide sample 2. Sample 2 had a pore range from 25 to 110 Å, a specific surface of 240 m²/g, and a maximum on the pore radius distribution at 45 Å.

TABLE

Expt. No.	Al ₂ O ₃ No.	Ni content, weight, %	H ₂ reduction time, hr	Specific surface, m ² /g	Pore size range, Å	Maximum on the pore volume distribution by radii in Å	Total C ₆ H ₆ absorbed at saturation, mmole/g	Cyclohexane dehydrogenation in % of theoret.
—	1	—	—	190	20—100	65	5,1	—
1	—	5	25	175	20—100	56	4,6	59,4
2	—	10	25	175	20—100	52	4,3	89,0
—	2	—	—	240	25—110	45	4,8	—
3	—	2	25	—	—	—	—	44,0
4	—	5	25	—	—	—	—	80,0
5	—	10	10	—	—	—	—	89,2
6	—	30	10	150	25—100	45	3,3	87,2
7	—	50	15	150	25—100	45	2,9	62,4
—	3	—	—	370	15—40	28	4,7	—
8	—	2	20	385	14—40	22	4,0	2,4
9	—	5	20	370	14—40	22	3,7	48,4
10	—	10	20	350	14—35	20	3,2	53,4
11	—	30	20	270	10—27	18	2,4	—

The table shows that when the amount of nickel was increased from 2 to 5%, the activity of the catalyst increased; the degree of cyclohexane dehydrogenation increased from 44 to 80.0% (experiments 3 and 4). An increase in the amount of nickel to 10% had comparatively little effect on the catalyst activity; the degree of cyclohexane dehydrogenation was 89.2% (experiment 5). As we showed previously, the activity of this catalyst remained practically constant during 600 hr of continuous operation [4]. The activity of the catalyst did not increase with an increase in the amount of nickel to 30%; the degree of cyclohexane dehydrogenation was 87.2%. With a further increase in the amount of nickel to 50%, the activity of the catalyst fell; the degree of cyclohexane dehydrogenation was 62.4% (experiment 7). It should be noted that this catalyst was also stable; its activity remained constant during 75 hr operation.

The adsorption data obtained show that catalysts containing 30 and 50% of nickel, which differed considerably in activity, did not differ in specific surface or the nature of the pore radius distribution, but had different total pore volumes, determined from the amount of benzene adsorbed on saturation. It is possible that the difference in the activity of these catalysts is explained not by the difference in the nature of their macrostructures, but by the change in dimensions of the nickel microcrystals and by the occurrence of side processes on the catalyst containing 50% nickel.

According to experimental data, the maximum catalyst activity on the two coarsely porous carrier samples was reached with 5-10% of Ni. This amount of nickel was apparently sufficient for the whole of the surface of these carriers accessible to cyclohexane to be filled.

It seemed interesting to determine how the activity of catalysts on finely porous aluminum oxide would change in relation to the amount of nickel deposited. Finely porous aluminum oxide 3 had the most developed surface of 370 m²/g, a pore radius range from 15 to 40 Å, and a maximum on the pore radius distribution at 28 Å. As the table shows, with an increase in the amount of nickel in the catalyst from 2 to 30%, the specific surface, the maximum on the pore radius distribution, and the volume of benzene adsorbed decreased. The data obtained showed that the catalyst with 2% nickel was inactive (experiment 8). Catalysts containing 5 and 10% nickel, obtained by reduction with hydrogen for 10-20 hr at 350°, were similar in activity; the degree of cyclohexane dehydrogenation was ~50% (experiments 9 and 10). The activity of the catalyst containing 30% nickel was not constant. In addition, considerable cracking was observed on this catalyst. Therefore little catalyzate was formed and the gaseous products contained ~35% of unsaturated hydrocarbons. The appearance of cracking properties for the catalyst with 30% nickel on finely porous aluminum oxide indicates that in this case a catalyst similar to nickel black was obtained.

SUMMARY

The properties of nickel-alumina catalysts with various nickel contents depend on the nature of the macrostructure of the aluminum oxide. Catalysts on coarsely porous aluminum oxide with 5 and 10% nickel have high and practically identical activities. The activity of a catalyst with 50% nickel is considerably lower. Catalysts on finely porous aluminum oxide with 5, 10, and 30% nickel have a low activity and are unstable.

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EFFECT OF SEPARATE STAGES OF THE POLYCONDENSATION
OF PRODUCTS FROM CATALYTIC DECOMPOSITION
OF ETHYL ALCOHOL ON THE CARON FORMATION RATE

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Translated from *Izvestiya Akademii Nauk SSSR*,

Otdelenie Khimicheskikh Nauk 1960, No. 1,

pp. 24-30, January, 1960

Original article submitted May 4, 1958

In previous work [1] we reported on the mechanism of carbon formation during the decomposition of ethyl alcohol on a copper-silica gel catalyst. According to this work, carbon formation, accompanying the decomposition of ethyl alcohol on the catalyst, consists of polycondensation of the alcohol decomposition products and alcohol itself; here two carbon formation mechanisms are possible, low-temperature one (up to 600°) and a high-temperature one (above 600°). In both mechanisms reaction cycles are repeated many times, leading to the same, increasingly higher-molecular products with a condensed, polycyclic structure (tars and carboids). In the low-temperature mechanism the acetaldehyde, which is first obtained from the alcohol, is polycondensed; in the high-temperature mechanism the original alcohol itself is polycondensed. In the first case the reaction cycles consist of two reactions, namely, condensation and dehydration; in the second case there are three reactions; namely, condensation, dehydration, and dehydrogenation; in both cases there are additional cyclization reactions after a definite number of cycles.

Thus, in the carbon-formation process there are many alternations of very simple reactions of a few types. All the reactions of one type, for example dehydrogenation or dehydration, may be combined in separate stages of polycondensation, the actual existence of which may be demonstrated experimentally by creating conditions for a selective effect on these stages. It seemed interesting to prove experimentally the existence of different polycondensation stages in the carbon formation process and also to show again the accuracy of the treatment proposed for the mechanism. It was advantageous to limit the investigation to conditions for realizing the low-temperature mechanism of carbon formation with the preliminary stage of catalytic dehydrogenation of alcohol.

EXPERIMENTAL

The investigation was carried out with exactly the same procedure as in our previous work [1], i.e., in an apparatus for heterogeneous catalytic investigations in a flow system with a detachable reactor, making it possible to determine the amount of carbon formed by direct weighing, described in [2-4]. Into the reactor was placed 10 ml (7.6 g) of the same catalyst as was used in the previous work [1], namely copper on silica gel with 0.0002 g of copper per g. The input space velocity of the reagent was 0.7 hr⁻¹. The ethyl alcohol used in the experiments was dried by distillation over calcium oxide [b.p. 78° (758 mm); d_{20}^{20} 0.7914, n_D^{20} 1.3620] and we also used mixtures of alcohol with acetaldehyde [b.p. 21° (760 mm)], distilled water, hydrogen, and ethylene. Experiments lasted for one hour. A fresh portion of catalyst was used for each experiment, with the exception of a special series with catalysts carbonized in previous experiments under analogous conditions. Experiments were carried out in the temperature range 200-600° and at atmospheric pressure.

One of the possibilities for a specific effect on separate stages of carbon formation, for example on dehydrogenation or dehydration, was the use of mixtures of alcohol with acetaldehyde, water, hydrogen and ethylene,

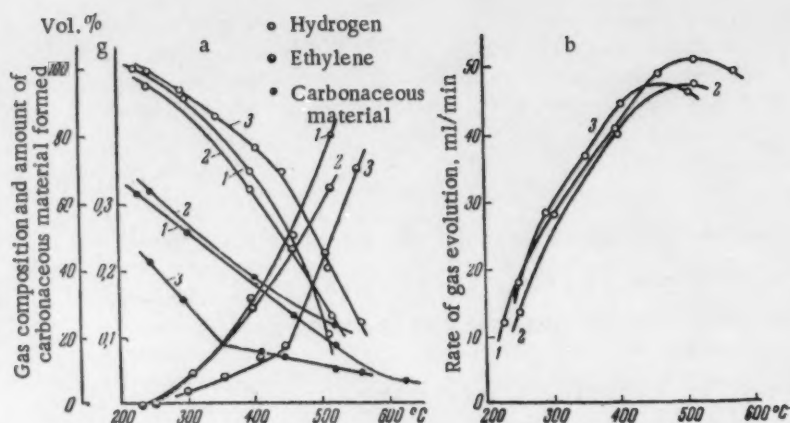


Fig. 1. Decomposition of pure ethyl alcohol and mixtures of it with 38.5 mol. % of acetaldehyde and 50 mol. % of water on a copper-silica gel catalyst: a) composition of reaction products; b) rate of contact gas evolution; 1) experiments with pure alcohol; 2) experiments with alcohol-aldehyde mixture; 3) experiments with alcohol-water mixture.

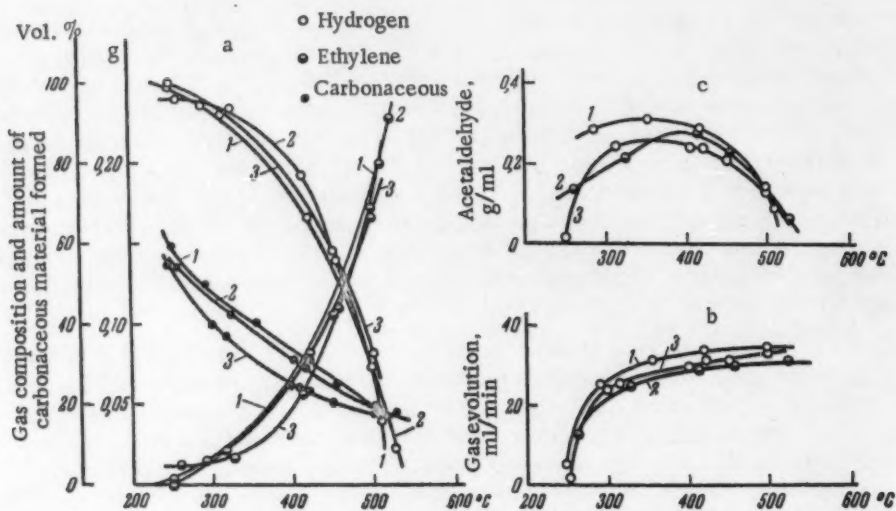


Fig. 2. Decomposition of pure ethyl alcohol and mixtures of it with 17.4 mol. % hydrogen and 19.5 mol. % ethylene on a copper-silica gel catalyst: a) composition of reaction products; b) rate of contact gas evolution; c) acetaldehyde content of catalyst; 1) experiments with pure alcohol; 2) experiments with alcohol-hydrogen mixture; 3) experiments with alcohol-ethylene mixture. In contrast to all the other experiments of the present work, in this series of experiments 5 ml of catalyst was taken with the previous reagent throughput rate, i.e., a space velocity of 1.4 hr^{-1} .

which are products of the reactions examined and could have an effect on their rate. Experiments with pure ethyl alcohol and mixtures of alcohol with 38.5 mol. % of acetaldehyde and 50 mol. % of water showed (Fig. 1) that the introduction of aldehyde into the mixture increased the carbon formation rate, while the introduction of water decreased it. The use of mixtures with less aldehyde and water lead to similar, but lesser effects. The increase in the carbon formation rate with the introduction of additional acetaldehyde is quite understandable, considering that in the case examined, the low-temperature carbon formation mechanism operates and here the

first stage is acetaldehyde formation. As Fig. 1 shows, the introduction of 38.5 mol. % of acetaldehyde into the reagent lowered the rate of alcohol dehydrogenation and dehydration comparatively little. Data on gas composition (Fig. 1, a) may be compared as the rates of the corresponding reactions, since the rates of gas evolution were practically identical in all the cases examined (see Fig. 1, b). As Fig. 1 also shows, the introduction of 50 mol. % of water into the reagent appreciably raised the dehydrogenation rate and very considerably reduced (by a factor of 2) the dehydration rate. In this case more aldehyde was obtained even than in experiments with pure alcohol, but despite this, the carbon formation rate was considerably reduced.

This apparent contradiction is actually explained by the fact that the strong retardation of the dehydration reaction affected not only the dehydration of alcohol, but also dehydration in cycles of successive conversions, leading to carbonaceous material, which reduced the carbon formation rate more strongly than it could be increased due to the increase in aldehyde concentration. Consequently, in the process examined, not only are factors accelerating or retarding the preliminary dehydrogenation of alcohol important, but also factors affecting the rate of dehydration reactions, which, according to the mechanism we adopted, are one of the stages of the carbon formation process. Thus, if the dehydration reactions become the most inhibited among the reactions of each cycle, then their rate limits the carbon formation rate. In this case, any change in the dehydration rate directly affects the carbon formation rate, while a change in the rate of the other reaction, namely, dehydrogenation, which is not limiting under the given conditions, has no effect.

An increase in the dehydrogenation rate in work with aqueous alcohol has been reported several times by different investigators [5-8], working, it is true, with mixtures containing less water than in the case we examined, and interpreted in a different way. Without dwelling on this problem, which is of specific interest, we will only note that the increase in the dehydrogenation rate with a simultaneous decrease in the carbon formation rate when aqueous alcohol mixtures are used makes it possible to improve practically the production of aldehyde from alcohol by increasing the rate of formation of the desired product, decreasing the loss of starting alcohol through dehydration and carbon formation, and increasing the working life of the catalyst without regeneration.

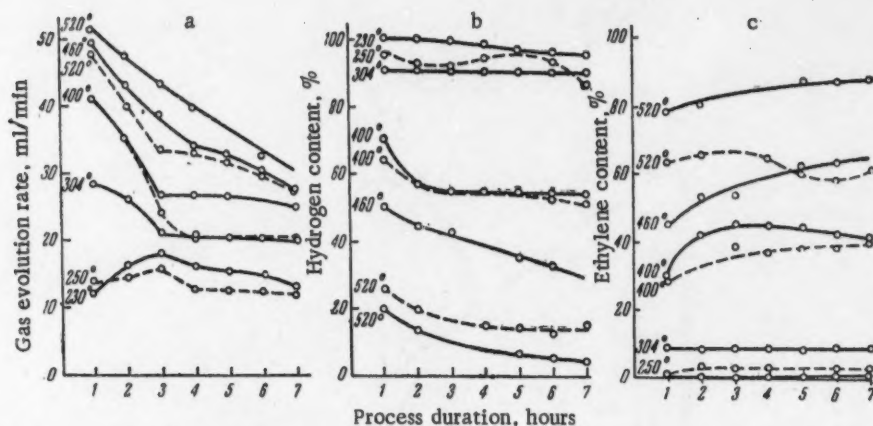


Fig. 3. Change in dehydrogenation and dehydration rates with time during the decomposition of pure ethyl alcohol and alcohol-aldehyde mixture (38.5 mol. %) on a copper-silica-gel catalyst: a) Rate of contact gas evolution; b) hydrogen content of contact gases; c) ethylene content of contact gases. The broken lines refer to experiments with alcohol-aldehyde mixtures.

Experiments with mixtures of alcohol with 17.4 mol. % of hydrogen and 19.5 mol. % of ethylene showed a decrease in the rate of carbon formation in comparison with experiments with pure alcohol (Fig. 2, a). In the case of an alcohol-hydrogen mixture, the fall in the carbon formation rate was insignificant. In the case of an alcohol-ethylene mixture there was a 20-25% fall in the carbon formation rate. Consequently, in this case also, retardation of the dehydration reaction had more effect in decreasing the carbon formation rate than retardation

of the dehydrogenation reaction. As Figs. 2, a, b, and c show, this difference is obtained because under the conditions of the catalytic dehydrogenation of alcohol, when dehydration reactions are weakly expressed and dehydrogenation reactions are strongly developed, the retarding action of ethylene extends mainly to the dehydration reactions, which are stages of carbon formation and limit it, while the retarding action of hydrogen extends to the dehydrogenation of alcohol to acetaldehyde, which, though it is the starting material for carbon formation, does not limit the latter as the aldehyde concentration in the reaction sphere remains quite high in this case. The retarding action of hydrogen and ethylene ceased to be appreciable at 500° (see Fig. 2, a and c).

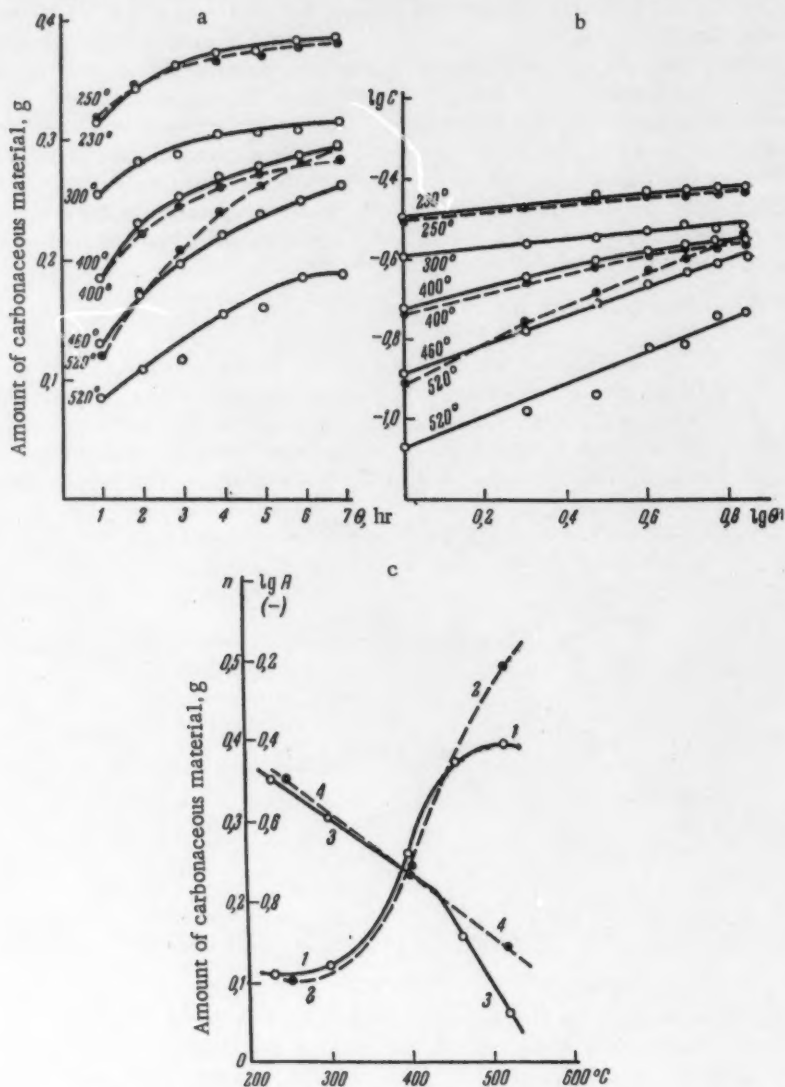


Fig. 4. Change in carbon formation rate during the decomposition of pure ethyl alcohol and alcohol-aldehyde mixture (38.5 mol. %) on copper-silica gel catalyst: a) course of carbon accumulation in the coordinates carbon mass-time; b) course of carbon accumulation in the coordinates log carbon mass-log time; c) changes in the coefficients n (curves 1 and 2) and log A (curves 3 and 4) with a rise in temperature. Broken lines refer to experiments with the alcohol-aldehyde mixture.

A prerequisite for the low-temperature carbon formation mechanism is preliminary catalytic dehydrogenation of alcohol to acetaldehyde, i.e., the catalyst plays a particularly active part in it. It was therefore interesting to examine the effect of increasing the carbonization of the catalyst and, consequently, the effect of shielding its active centers with carbonaceous material on the rate of dehydrogenation and carbon formation. In Fig. 3 we compare the results of 7-hr experiments with pure alcohol and alcohol-aldehyde mixture (38.5 mol. % of acetaldehyde) on a copper-silica gel catalyst after each hour.

As Fig. 3, a shows, curves of the change in gas evolution rate, i.e., the over-all rate of the dehydrogenation and dehydration reactions, both in experiments with pure alcohol and with the alcohol-aldehyde mixture, show a break after 3-4 hours operation of the catalyst. By comparing this with the distribution of the over-all reaction rate between dehydrogenation and dehydration rates separately, which can be assessed sufficiently accurately from the hydrogen and ethylene contents of the contact gas (see Fig. 3, b and c), we may characterize the change in reaction rates in relation to the operating time of the catalyst without regeneration in the following way. At 250°, during the first 3 hours operation, there is an increase in the dehydrogenation rate by a factor of 1.5, but in the next 4 hours, a decrease. At 300-400°, there is a decrease in the dehydrogenation rate by a factor of 1.5 in the first 3 hours and then the rate remains constant for the next 4 hours. At 460-520°, there is a decrease in the dehydrogenation rate by a factor of 2 over the whole 7 hours operation with a more or less clearly expressed break in the curves after 3-4 hours. No similar change in the dehydration rate occurs over the temperature range studied. During the whole of the operating time of the catalyst, the dehydration rate had some definite value, characteristic of the given temperature.

Thus, in the first 3-4 hours operation, carbon deposition on the catalyst surface at 250° leads to an increase in the activity of the catalyst for dehydrogenation; subsequent carbon deposition reduces the activity of this carbonized catalyst again to approximately the original value. At 300-400°, carbon deposition reduces the original activity of the catalyst for dehydrogenation by a factor of 1.5 and then the activity remains constant during the next 4 hours. At a temperature above 400° there is a gradual fall in the catalytic activity for dehydrogenation over the whole 7 hours operation. In the latter case there is apparently actual shielding of the active centers of the catalyst by carbon. These observations confirm the results of previously published work in which the formation of "carbonaceous dendrites" was reported [9-11].

As Fig. 4, a and b, shows, curves of carbon accumulation for experiments with pure alcohol and the alcohol-aldehyde mixture at 230-400° almost completely repeat each other, while at 520° the curve for the alcohol-aldehyde mixture goes considerably higher and the difference between the curves increases with an increase in the duration of the process.

In Fig. 4, b, the carbon accumulation curves are plotted in the coordinates of $\lg C$ against $\lg \Theta$, in which they are straight lines obeying the equation

$$\lg C = \lg A + n \lg \Theta,$$

where C is the amount of carbonaceous material accumulating in time Θ , Θ is the duration of the experiments in hours, n and A are coefficients depending on temperature, and A is the amount of carbonaceous material formed in the first hour of operation.

The values of the coefficients n and $\log A$ in relation to temperature are presented in Fig. 4, c. As this figure shows, their values for experiments with pure alcohol and a mixture of alcohol and 38.5 mol. % of acetaldehyde are practically identical up to a temperature of 430°, above which they deviate considerably. From this one can conclude that the limit of the above-mentioned differences in the course of the carbon accumulation curves for experiments with pure alcohol and the alcohol-aldehyde mixture may be defined accurately as 430°. Below this temperature no differences are observed in the rates of carbon formation when pure alcohol and the alcohol-aldehyde mixture are used. Above this temperature there are differences, which are greater the higher the temperature.

The phenomena observed are evidently explained by the fact that with a decrease in the alcohol dehydrogenation rate as the temperature increases, the preliminary dehydrogenation of alcohol to acetaldehyde becomes increasingly the limiting stage of the carbon-formation process. At temperatures below 430° the degree of conversion of alcohol into aldehyde is greater than 38.5% and therefore at these temperatures the introduction of

aldehyde into the alcohol has no effect on the carbon formation rate. At temperatures above 430°, on the other hand, the degree of conversion of alcohol into aldehyde is below 38.5% and therefore the aldehyde introduced has an ever-increasing effect on the carbon formation rate with a rise in temperature.

Thus, retardation of the dehydrogenation reaction affects the carbon-formation rate. In previous examples with alcohol-water and alcohol-ethylene mixtures, the cases where retardation of the dehydration reactions affected the carbon-formation rate were examined. This confirms the accuracy of the low-temperature mechanism proposed in the previous work [1] for carbon formation during the decomposition of ethyl alcohol on a catalyst, and also demonstrates the existence of the separate elementary stages constituting this process. As regards the other elementary stages of the carbon-formation process, namely, condensation and cyclization, under certain conditions they evidently also can become the limiting stages of carbon formation and acceleration or retardation of them would produce acceleration or retardation of the carbon-formation process.

SUMMARY

1. There are separate stages in the process of carbon formation during catalytic decomposition of ethyl alcohol (dehydrogenation and dehydration) and retardation or acceleration of these produces a decrease or an increase in the carbon formation rate.
2. The effect of the separate stages on the whole carbon formation process is observed only under conditions when the reactions of these stages are hindered and become limiting.
3. The material obtained confirms the representation of the mechanism of carbon formation during ethyl alcohol decomposition as a multistage polycondensation of reaction products and representation of the low-temperature mechanism as a process passing through preliminary dehydrogenation of alcohol.

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*Original Russian pagination. See C. B. translation.

POLYMORPHISM AND CATALYTIC PROPERTIES OF Al_2O_3

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Translated from *Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh*
Nauk 1960, No. 1, pp. 31-38, January, 1960
Original article submitted May 5, 1958

At the present time there is no doubt that apart from corundum and $\gamma\text{-Al}_2\text{O}_3$ there exists a series of other phases or polymorphic modifications. These, and their x-ray diffraction patterns are quite reproducible. In the last decade a series of papers [1-8] has been devoted to the structural investigation and study of the formation conditions of Al_2O_3 phases, of which there is a total of not less than six. There is a certain arbitrariness in the nomenclature of Al_2O_3 phases and investigators of different schools have frequently denoted the same phases by different symbols. The catalytic activity has not been studied in any of the work mentioned. Since the structures of the crystals of these phases differ (though they have not been established accurately as yet [4]), from the point of view of studying the structural factor in catalysis, it seemed interesting to determine their catalytic dehydration activity and this we did for the decomposition of $\text{i-C}_3\text{H}_7\text{OH}$. Below we denote the different Al_2O_3 phases in accordance with the system adopted in [3, 8, and 9].

EXPERIMENTAL

For the investigation undertaken, it was very important that the catalysts did not contain traces of foreign materials. The aluminum hydroxide was therefore precipitated with ammonia; the NH_4NO_3 adsorbed on it decomposed completely to H_2O and N_2O when heated above 360° . All the catalysts were prepared from the same sample of aluminum nitrate (analytical grade), containing not more than 0.0025% of heavy metals. We obtained boehmite, AlOOH by precipitation from 10% aluminum nitrate solution with 10% ammonia at the boiling point over a period of an hour; the precipitate was washed with hot water and, as in all the other cases, the pure hydroxides were collected by filtration, formed, and dried at 110° . Hydrargillite, $\text{Al}(\text{OH})_3$, was prepared analogously, but at room temperature, and was washed with cold water. Bayerite, $\beta\text{-Al}(\text{OH})_3$, was precipitated at $60\text{-}80^\circ$. In addition, a gel with NH_4NO_3 was prepared by rapid mixing of concentrated solutions of $\text{Al}(\text{NO}_3)_3$ and NH_4OH in the cold and sucking off without washing. The formation of all these substances was checked by x-ray methods. Pastes of the hydroxides were formed by passage through the dies of a press; after their conversion into oxide, the catalyst particles had a cross section of $1.1\text{-}1.3\text{ mm}^2$. Two methods were used for conversion of the hydroxides into oxides: 1) heating in air in a Pt crucible and 2) heating in the presence of steam in a specially constructed quartz vessel. The Pt crucible with the hydroxide was placed in a crucible furnace, the internal temperature of which was measured with a Pt-PtRh thermocouple and which was first heated to the given temperature. After being fired in an H_2O atmosphere, samples were rapidly cooled without access to moist air. Information on the Al_2O_3 phases prepared is given in Table 1; in addition, we also prepared and investigated a series of corundum preparations, to whose investigation article [10] was devoted. As the data in Table 1 show, we obtained several preparations for each of several Al_2O_3 phases and depending on the preparation method, they contained various amounts of residual water, which we determined by firing to constant weight at 1100° , and differed considerably in the specific surface s .

The x-ray investigation of the phases was carried out in PRK cameras with filtered (Ni) Cu K radiation by both symmetrical and unsymmetrical registration methods so as to obtain more accurate values of the interplanar

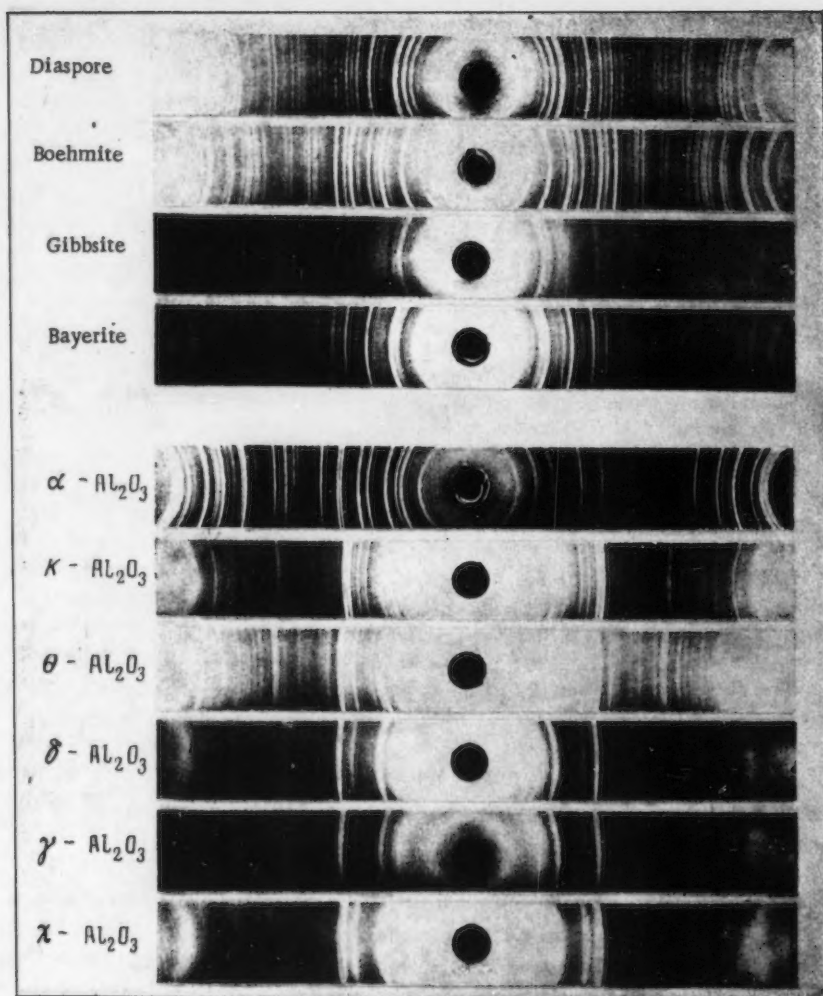


Fig. 1. X-ray patterns of original hydroxides and the Al_2O_3 phases obtained from them.

distances. X-ray patterns of the original hydroxides and the Al_2O_3 phases obtained from them, registered by the symmetrical method, are given in Fig. 1 and the results of phases analysis, in Table 1; for the latter we used tabular data (values of d and I) from [1-9]. The crystal dimensions were calculated from the half-widths of the reflections, determined from microphotometric curves, obtained with an MF4 microphotometer. As Fig. 1 shows, the x-ray patterns of the χ - and γ -phases had a small number of broad lines, which in the first case were indexed as lines of a primitive cubic lattice, and in the second case, as a face-centered lattice. The average dimensions of the crystals of these phases were of the order of 50 Å. The other phases were characterized by a considerably larger number of lines, retaining a high dispersion with crystal dimensions of the order of 100 Å. X-ray patterns of the phases after catalytic experiments had been carried out on them for 15-20 hr did not differ from the corresponding x-ray patterns obtained before the experiments.

The specific surface S , and the total volume V and diameter \bar{d} of the pores were determined from isotherms of benzene vapor adsorption at 20°, measured on an apparatus with MacBain quartz balances. The benzene, which had been distilled over sodium, was pumped out in an ampoule until air had been removed completely. Before the beginning of measurements, samples (200-700 mg) were pumped out at 300° to constant weight. The sensitivity of various balances was within the range 2-8 mg/mm. The adsorption isotherms were measured over the

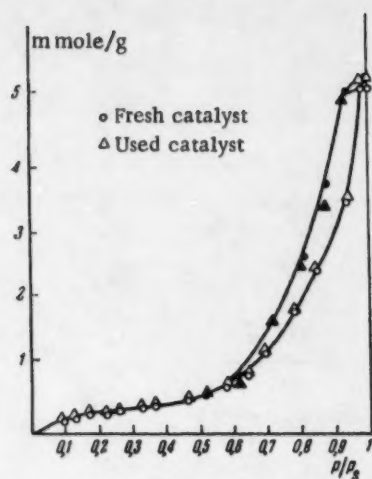


Fig. 2. Isotherms of Θ - Al_2O_3 preparation.

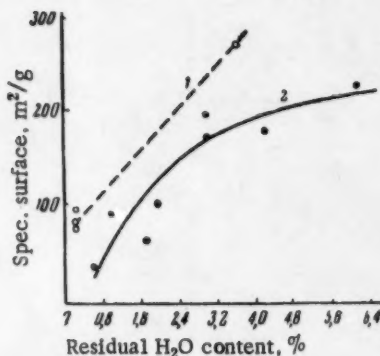


Fig. 3. Effect of residual water in Al_2O_3 on the surface size: 1) thermal treatment in air; 2) thermal treatment in H_2O vapor.

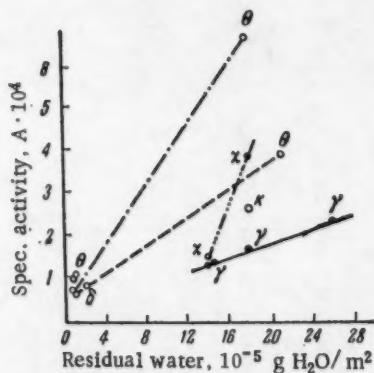


Fig. 4. Relation between specific activity and $\alpha \text{H}_2\text{O}$.

p/p_s range from 0.01 to 1.0. The value of S was calculated from the BET equation, d from the Kelvin equation without a correction for the adsorption layer, and V from the amount of adsorption at $p/p_s \approx 1$. The results of the measurements are given in Table 1. As an example, Fig. 2 shows isotherms measured on fresh (circles) and used (triangles; black symbols represent desorption) Θ - Al_2O_3 preparation (preparation C): Their coincidence shows the absence of appreciable changes in the adsorption characteristics during catalytic experiments and this is readily explained by the low reaction temperature.

The catalytic activity was determined for dehydration of absolute isopropyl alcohol at 245° and, in a few cases, at 260° also, and at space velocities of 1 and 1.7 hr^{-1} in a flow system. The catalyst volume was 3 cc in all experiments. During the reaction the temperature was measured with a thermocouple in the center of the catalyst bed. According to gas analysis data, obtained on a GIAP apparatus, the sole gaseous reaction product was propylene, i.e., only dehydration occurred.

The gas evolution was steady during the experiments, making it possible to calculate the reaction rate constants from formula $k = \frac{N \cdot m}{M - m/2}$ (11). Together with the degrees of conversion, which characterize the over-all activity, these data are given in Table 1; this table shows that for each phase, the values of k at different space velocities agreed quite satisfactorily. Analogous data for experiments at 260° are contained in Table 2. Tables 1 and 2 also contain data on the values of the specific activity $A_{\text{spec}} = k/s$, expressed in $10^4 \text{ mole/m}^2 \cdot \text{min}$. For the comparison of different preparations, this expression A_{spec} required the calculation of the H_2O content per m^2 of surface ($\alpha \text{H}_2\text{O}$); these data are given in the last column of Table 1.

In addition to the phases described in Table 1, by prolonged firing of hydrargillite at 1100° we obtained corundum, α - Al_2O_3 , with S $13 \text{ m}^2/\text{g}$, V 0.35 cc/g , and $d > 500 \text{ \AA}$. It was completely inactive at 245 and 260° , but at 300° it was possible to measure the rate of the reaction on it and to determine A_{spec} , which was found to be of the order of $10^{-6} \text{ mole/m}^2 \cdot \text{min}$, i.e., 2 orders less than for the other phases.

DISCUSSION OF EXPERIMENTAL RESULTS

An examination of literature data and also data presented in Table 1 shows that the structure of the original hydroxides has a strong effect on the formation of Al_2O_3 phases in addition to the thermal dehydration conditions. There are actually three series of phase conversions:

1. Hydrargillite $\rightarrow \chi(k', \epsilon)\text{-Al}_2\text{O}_3 \rightarrow k\text{-Al}_2\text{O}_3 \rightarrow \alpha\text{-Al}_2\text{O}_3$
2. Bayerite } $\rightarrow \gamma(\gamma)\text{-Al}_2\text{O}_3 \rightarrow \delta\text{-Al}_2\text{O}_3 \rightarrow \Theta\text{-Al}_2\text{O}_3$
- Boehmite }
3. Diaspore $\rightarrow \alpha\text{-Al}_2\text{O}_3$

TABLE 1

Al₂O₃ Phases and Their Dehydrating Activity in the Catalytic Decomposition of i-C₃H₇OH

Preparation method	Phase by x-ray data	Bulk wt. g/cc	H ₂ O con- tent, %	Spe- cific sur- face, m ² /g	Total pore volume V in cc/g	Pore di- ameter d _p in Å	i-C ₃ H ₇ OH conver- sion at 245° in %		Rate constant at 245°		A _{spec} 10 ⁴		Adsorbed water in H ₂ O in g/m ²
							Space velocity	1 hr ⁻¹	Space velocity	1 hr ⁻¹	Space velocity	1 hr ⁻¹	
From hydrargillite at 470° in H ₂ O vapor atmosphere, 1 hr	χ, prep. A	0,9	3,0	197	0,289	55	80,0	73,3	0,08	0,12	1,45	2,2	0,00015
From hydrargillite at 750° in H ₂ O vapor atmosphere, 1 hr	χ, " B	0,9	1,9	100	0,303	95	94,0	83,0	0,1	0,14	3,8	5,3	0,00019
From bayerite at 470° in air, 1 hr	γ, " A	0,58	3,7	274	>0,500	20-300	69,0	52,0	0,06	0,07	1,35	1,45	0,00013
From bayerite at 550° in H ₂ O vapor atmosphere, 1 hr	γ, " B	0,64	3,14	220	>0,52	20-300	64,4	51,0	0,06	0,07	1,35	1,6	0,00015
From gel with NH ₄ NO ₃ at 550° in H ₂ O vapor atmosphere, 1 hr	γ, " C	0,78	6,13	225	0,330	65	35,8	30,5	0,03	0,04	0,5	0,7	0,00027
From boehmite at 700° in H ₂ O vapor atmosphere, 1 hr	γ, " D	0,75	4,15	159	0,520	95	80,5	—	0,07	—	2,25	—	0,00026
From boehmite at 700° in air, 3 hr	γ, " E	0,8	0,9	92	0,300	85	64,3	55,5	0,06	0,08	2,58	3,48	0,0001
From boehmite at 1000° in H ₂ O vapor atmosphere, 1 hr	θ, " A	0,8	1,72	85	0,460	145	79,2	55,0	0,08	0,08	3,9	4,0	0,00024
From bayerite at 900° in H ₂ O vapor atmosphere, 1 hr	θ, " B	0,58	1,04	60	0,152	125	78,7	50,0	0,07	0,07	6,8	6,4	0,00017
From bayerite at 1100° in air, 3 hr	θ, " C	0,57	—	71	0,465	75 и 175	15,5	14,0	0,01	0,01	0,82	1,2	<0,00002
From boehmite at 1100° in air, 6 hr	θ, " D	0,86	—	84	0,390	115	23,8	—	0,02	—	0,77	—	<0,00002
From hydrargillite at 1000° in H ₂ O vapor atmosphere, 1 hr	z	0,9	0,63	34	0,350	~370	32,5	48,0	0,02	—	2,58	—	0,00018
From gel with NH ₄ NO ₃ at 1000° in air, 6 hr	δ	0,91	0,2	89	0,293	95	Inactive	—	—	—	—	—	0,00002

TABLE 2

Data on $i\text{-C}_3\text{H}_7\text{OH}$ Decomposition at 260°

Phase	Degree of conversion, %		Rate constant		$A_{\text{spec}} \cdot 10^4$	
	space velocity 1	space velocity 1.7	space velocity 1	space velocity 1.7	space velocity 1	space velocity 1.7
γ_c	82,8	66,5	0,08	0,08	1,5	1,8
δ	82,9	88,3	0,08	0,08	9,0	14,8
α	12,0	—	0,08	—	0,9	—

where we give other symbols encountered for analogous phases in brackets. We should also add that as hydrargillite forms boehmite during slow dehydration, γ - and Θ - Al_2O_3 may also be obtained from hydrargillite under certain conditions. The ready reproducibility of Al_2O_3 phases under different conditions is a demonstration of their crystallochemical individuality, though it is not clear as yet how much their crystal lattices differ from each other in structure. This uncertainty served as basis for the hypothesis that all the intermediate phases of Al_2O_3 are morphologically different preparations of γ - Al_2O_3 , which was put forward by Frary [12] and disproved by subsequent detailed structural investigations [1-9]. We have already noted above that the structure of the phases did not change during catalytic experiments. As the data in Table 1 show, the residual water content was not a characteristic of any phase. Actually, χ - Al_2O_3 we obtained under various conditions contained 1.9 and 3.0 % of H_2O , γ - Al_2O_3 0.9-6.1%, and Θ - Al_2O_3 from 0.1 to 1.7%. The amounts of H_2O per m^2 of surface also differed considerably (Table 1). Thus, it is clear that the existence of phases or polymorphic modifications of Al_2O_3 is not caused by differences in the amounts of water remaining in them. Each of them gave the same x-ray pattern, regardless of the H_2O content. This was also confirmed by the constancy of the x-ray patterns during an increase in H_2O content during catalytic experiments.

However, the H_2O content affected the physical structure; a comparison of data on its content and values of S shows (Fig. 3) that the latter increased with an increase in H_2O content over the range studied both in preparations obtained in air and in a water-vapor atmosphere. In addition, Table 1 shows that the residual water content was a function of temperature; the higher the latter under otherwise equal treatment conditions, the smaller was the residual H_2O content. This result is in good agreement with the conclusions in [13], in which the adsorption properties of Al_2O_3 were studied. It should also be noted that samples with a lower H_2O content had larger pores. However, the latter circumstance can hardly affect the activity, as in general all the catalysts we examined were not finely porous, but had pores whose diameter was many times greater than the diameter of an isopropanol molecule. Therefore, it can be assumed that the whole of the measured surface S was available for reaction and that the observed differences in activity were not caused by differences in the porous structure of the different phases or different preparations of the same phase. In confirmation of this, we should point out that preparations D and E of γ - Al_2O_3 , δ - Al_2O_3 , and preparation B of χ - Al_2O_3 had pores of the same diameter, but their total and specific activities were different.

All that has been said above compelled us to approach the evaluation of the comparative activities of the Al_2O_3 phases with great care and we concluded that it was only possible to compare preparations of different phases in which $a_{\text{H}_2\text{O}}$ was the same; in Fig. 4 we plotted the values of A_{spec} for a space velocity of 1 hr^{-1} against $a_{\text{H}_2\text{O}}$.

We grouped the catalysts according to water content in such a way that one group contained samples for which $a_{\text{H}_2\text{O}}$ differed by not more than $\pm 0.00001 \text{ g}$, except in the case of Θ_A and γ_D , and in constructing the graph we used the average value of $a_{\text{H}_2\text{O}}$ for each group, for example, catalysts with 0.17 - 0.19 mg/m^2 belonged to the group with 0.18 mg/m^2 . A similar picture was also obtained for experiments with a space velocity of 1.7 hr^{-1} . An examination of Fig. 4 leads to the following results: 1) Arrangement of Al_2O_3 phases according to A_{spec} gives the series $\Theta > \chi > \kappa > \gamma > \alpha$, as can be seen from the group with 0.18 mg/m^2 , which contains the greatest number of phases, and from data presented in the experimental part for α - Al_2O_3 . This result is also confirmed by the relative activity of the phases at 0.14 and 0.22 - 0.26 mg/m^2 . The separate position of samples with a very low water content, including the δ -phase, is readily explained, as below, from the point of view of the state of water in Al_2O_3 . For the present, it should be stated that Al_2O_3 phases are characterized not only by different crystal structures, but also differ somewhat in their specific catalytic activities.

2) As we obtained several preparations of some Al_2O_3 modifications, we were able to evaluate the change in catalytic activity with the residual water content in a given Al_2O_3 phase. This effect was seen particularly clearly in the case of γ - Al_2O_3 and was repeated in principle for the Θ - and χ -phases. Over the H_2O content range investigated, the catalytic activity increased with the water content, $\alpha_{\text{H}_2\text{O}}$. This is of great importance as it indicates the nature of the active centers in the catalysts studied. First of all, we should note that in our case the maximal H_2O content in general corresponds to the capacity of 1 m^2 of surface for OH groups, i.e., $\alpha_{\text{OH}}^{\text{m}} \approx 1.3 \text{ mg-equiv/g}$. This means that in the limit all the water can be present in the catalysts in the form of OH groups. Thus, the increase in A_{spec} with an increase in $\alpha_{\text{H}_2\text{O}}$ is readily explained if we assume that OH groups are more active as dehydration centers than oxygen atoms. At very low residual H_2O content, A_{spec} was found to be very low, probably due to the fact that the concentration of OH groups on the surface of the catalysts was very low. In the evaluation of the activity of the δ -phase, this fact could be of great importance and therefore we did not include it in the series presented above.

Although, as was said at the beginning of the article, there is no literature on the activity of Al_2O_3 phases intermediate between amorphous alumina and corundum (with the exception of γ - Al_2O_3 , which, in the light of what has been said above, was not the same in different work), the effect of thermal treatment on Al_2O_3 has been studied repeatedly. Thus, Fricke and Wessing [14] investigated the effect of firing at 600 - 800° on the total activity and found that it fell with an increase in the firing temperature and duration. Antipina and Frost [15] studied these changes over the range 400 - 1200° and showed that with firing at up to 500° the total activity increased; at 500 - 800° it did not change; and with firing at 1200° , it fell sharply. Brey and Krieger [16] determined the change in specific activity of one industrial sample of Al_2O_3 catalyst and found that firing at 900° gave a lower specific activity than firing at 600° . This is contradictory to the results of our investigation presented above, in which the Θ -phase, obtained at temperatures close to the transition point of corundum, had the highest specific activity and also to the results of Boreskov and his co-workers [17]. By studying the effect of thermal treatment on three Al_2O_3 samples, these investigators found that when Al_2O_3 was fired within the range 450 - 1200° , A_{spec} increased somewhat up to 1000° and fell sharply at 1200° . According to their data, the over-all activity did not depend on firing temperature up to 600° , but fell with a further rise in temperature.

In connection with the work cited [14-17], the following remarks may be made: 1) The existence of phases differing in structure both from γ - and also from α - Al_2O_3 was not considered in any of them; 2) neither the residual water content nor its effect on total and specific activity was determined; 3) the experiments on alcohol decomposition were carried out at high temperatures. As the data of our investigation show, for studying the comparative activity of phases it is more convenient to work with isopropyl alcohol as the reaction with it proceeds at a high rate even at temperatures 130 - 170° lower than in the work cited. Isopropyl alcohol is also a more convenient material from the point of view that the possibility of partial cracking is excluded at the lower temperatures.

If we ignore studies of the reaction temperature, the most similar investigation to ours is the work of Boreskov and his co-workers [17]. Both they and we found an increase in A_{spec} , determined as K/s with firing temperature up to 1000° . However, in [17] this was hypothetically explained thus: With high-temperature treatment, the very fine pores, which are not used in the very rapid reaction at 420° , disappeared; while in our work this phenomenon was explained by phase conversions of Al_2O_3 and the different activities of the phases with allowance for the residual water content, as given above. Moreover, approximately the same data on the specific activity of corundum prepared at high temperatures were obtained by the authors of [17] and by us. In experiments at 350° with it, we also observed dehydrogenation of alcohol at 350° . Boreskov and his co-workers explained this by concentration of impurities on the corundum surface during the decrease in surface in the formation of corundum from γ - Al_2O_3 . It is possible that this also occurred in our case, though we reduced the amount of impurities to a minimum by precipitating the hydroxide with ammonia. We observed cracking on a sample of corundum which contained impurities introduced during its preparation [10] as the emergent reaction gases contained a certain amount of methane. As regards the total activity of the Al_2O_3 phases, as can be seen from all the data we presented, it changed in the same direction as the size of the catalyst surface; in addition, the water content of the Al_2O_3 affected it.

SUMMARY

1. Together with γ - and α - Al_2O_3 , other polymorphic modifications of Al_2O_3 described in the literature (χ , κ , Θ , and δ phases) were also prepared and it was shown that their existence is not caused by differences in the residual

water content of the aluminum oxide and their total and specific activities in the catalytic dehydration of iso- C_3H_7OH were determined for the first time.

2. The total catalytic activity of the phases changed symbatically with a change in the specific surface. According to the specific activity, found for preparations with the same residual water content per m^2 of surface, the phases form the series $\Theta > \chi > \kappa > \gamma (< \delta) >> a$. It was shown that A_{spec} of some phases obtained at high temperatures was higher than that of those obtained at low temperatures.

3. It was confirmed that there are three series of phase conversions, depending on the nature of the original aluminum hydroxides.

4. It was established by x-ray methods that the phases retained their structural characteristics during catalytic experiments.

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CRYSTAL STRUCTURES OF TROPYLIUM PERCHLORATE AND IODIDE

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Translated from *Izvestiya Akademii Nauk, SSSR,*
Otdelenie Khimicheskikh Nauk 1960, No. 1. pp.

39-44, January, 1960

Original article submitted April 30, 1958

The purpose of our x-ray structural investigation of the given salts was the elucidation of the structure of the new aromatic system, the tropylium cation $C_7H_7^+$, as the literature contains only preliminary x-ray data on its chloride C_7H_7Cl [1], whose structure could not be determined due to its complexity.

Crystals of the iodide [2] and perchlorate [3] obtained from aqueous solution were highly elongated hexagonal prisms (needles). By the oscillation method and photographing the reciprocal lattice, it was established that the crystals belonged to the hexagonal syngony and the parameters of the elementary cells (the corresponding rhombohedral cells contain one molecule each) were determined:

	$[C_7H_7][ClO_4]$	$[C_7H_7]I$
$a = b(\text{\AA})$	$9,39 \pm 0,04$	$9,01 \pm 0,02$
$c(\text{\AA})$	$8,54 \pm 0,04$	$8,22 \pm 0,02$
$V(\text{\AA}^3)$	652	578
$d_{\text{meas.}}, \text{g/cc}$	$\sim 1,4$	$\sim 1,8$
$d_{\text{x-ray}}, \text{g/cc}$	1,46	1,89
M	190,6	218,05
n	3	3

The two compounds were characterized by identical systematic extinctions, leading to the three possible space groups $D_3^7 = R32$; $C_3^5v = R3m$; and $D_3^5d = R\bar{3}m$, in which the multiplicity 3 corresponds to positions with symmetry 32 , $3m$, and $\bar{3}m$, respectively. The natural symmetry of the perchlorate ion, $4\bar{3}m$, is only compatible with the symmetry $3m$, so that tropylium perchlorate belongs to the space group $C_3^5v = R\bar{3}m$ (the centrosymmetrical group D_3^5d is also excluded by the considerable piezo effect). Such a crystallochemical choice of the space group is impossible for the iodide due to the spherical symmetry of the iodide ion, but the weak piezo effect apparently also eliminates the group D_3^5d , leaving the two possibilities $D_3^7 = R32$ and $C_3^5v = R\bar{3}m$.

In both crystals the tropylium ion occupies a position with multiplicity 3, the symmetry of which ($3m$ or 32) apparently does not correspond to the inherent symmetry of a seven-membered ring (for example, $7/mmm$ with coplanarity and equal C-C bond lengths). Consequently, the statistical disorder of the $C_7H_7^+$ ions in the crystal is quite evident and consists of arbitrary rotation around axis 3, due to which the tropylium ion imitates the symmetry of a cylinder. This disorder weakens the x-ray analysis results and, in particular, makes it impossible to determine the individual values for the C-C bond lengths.

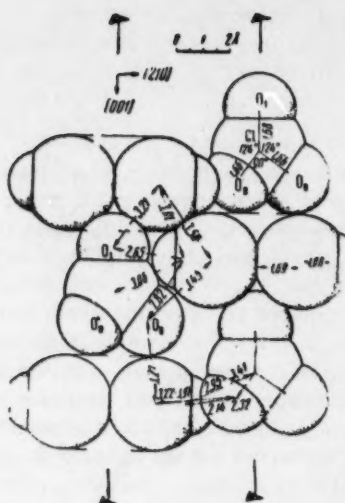


Fig. 1. Anion-cation contact points in the tropylium perchlorate structure.

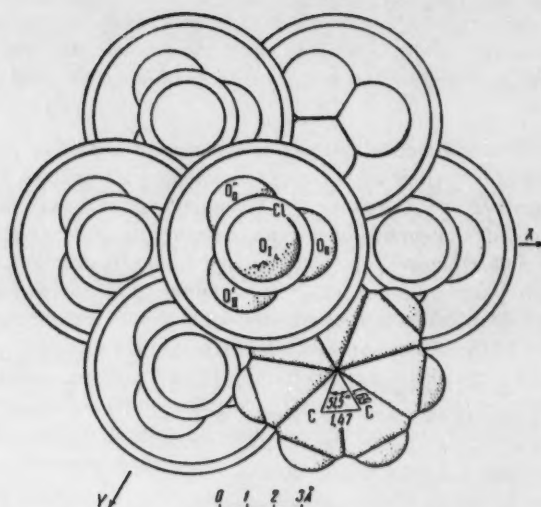


Fig. 2. Projection xy of the tropylium perchlorate structure.

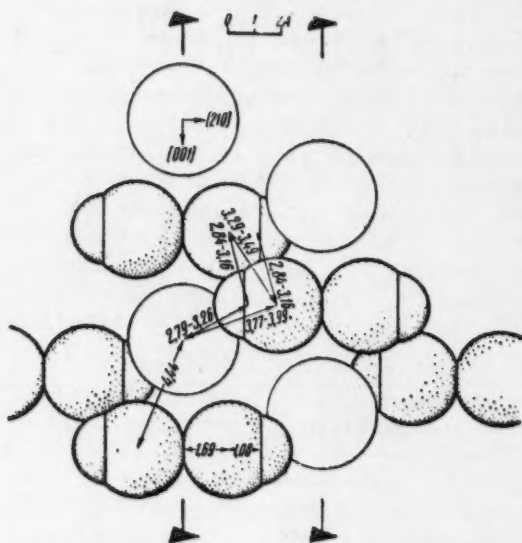


Fig. 3. Packing of ions in the tropylium iodide structure.

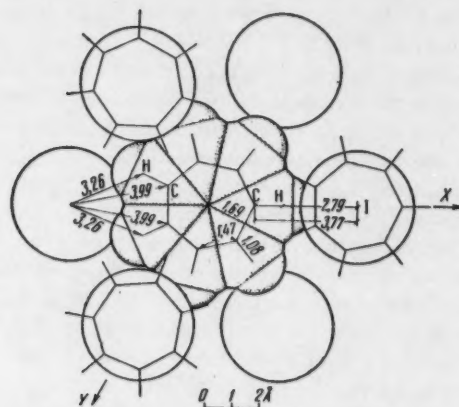


Fig. 4. Cation-anion contacts in the tropyllium iodide structure.

of hk0, hk1, hk2, hk3, hk4, hk5, hk6, 0kl, and 1kl). The F^2 series of the perchlorate clearly showed maxima which corresponded to two independent Cl-O vectors and an annular maximum from the Cl-C vectors. This maximum had a relatively constant height along the whole circumference, which indicates the absence of pre-dominating cation orientations (a certain increase in the height of the symmetry planes is due to superposition of Cl-O maxima). Taking the Cl atom as the origin of the coordinates, we obtain:

	<i>x</i>	<i>y</i>	<i>z</i>
Cl	0	0	0
O _I	0	0	0,197
O _{II}	0,144	0	-0,112
C	0,180	0	-0,486

The F^2 series of the iodide showed, besides a trivial maximum, only an annular maximum that was constant in height along the circumference and corresponded to the I-C vectors.

	x	y	z
C	0 0,188	0 0	0 0,500

The radius of the annular maximum was the same in the two structures and equaled 1.69 ± 0.03 Å. If we assume coplanarity of the tropylium cation and equality of the bond lengths, this gives $C-C = 1.47 \pm 0.03$ Å. If there is a deviation from coplanarity it cannot exceed 0.1 Å as the ring maximum is quite narrow in the z direction. If the bond lengths are unequal, then the value 1.47 Å should be close to their mean value.

The perchlorate ion configuration is as follows: $Cl-O_I = 1.68$ Å (bond along axis 3) $Cl-O_{II} = 1.66$ Å; $O_I-Cl-O_{II} = 124^\circ$; $O_{II}-Cl-O_{II} = 90^\circ$.

Quite contradictory and inaccurate data are given in the literature [4] on the Cl-O bond length in different perchlorates and these vary from 1.4 to 1.6 Å. The value we found was close to the sum of the covalent radii, 1.65 Å. Considerable distortion of the valence angles causes an increase in three of the six O---O inside the anion to 2.94 Å and a decrease in the other three to 2.35 Å; with tetrahedral angles and the experimental value of the Cl-O bond length, all six O---O distances are the same and equal 2.71 Å. Such anion deformation may be explained reasonably by packing peculiarities (see below).

The perchlorate structure consists of polar columns of alternating anions and cations along axis 3 (Fig. 1) with each cation (anion) touching both the upper and lower anions (cations) at equal distances: $C_I \cdots C = O_{II} \cdots C = 3.21$ Å. Each column is surrounded by six adjacent ones so that the structure consists of hexagonal packing of these columns (Fig. 2) and this was found to be as densely packed as the columns themselves. Each cation of a given column touches six cations from adjacent columns (3 above and 3 below) and, depending on the relative rotation of the cations, the shortest distances between them vary over the following ranges: $C \cdots C = 3.50-3.68$; $C \cdots H = 3.01-3.33$ Å. In addition, each cation touches six anions of adjacent columns (3 above and 3 below), so that the coordination number of a cation and an anion equals 12. The shortest distances between a cation and a lower anion (Fig. 1) vary over the ranges: $O_I \cdots H = 2.65-3.16$ and $Cl \cdots H = 3.06-3.51$ Å. The contact between a cation and an upper anion is interesting. If a projection of the tilted $Cl-O_{II}$ bond of the anion onto the xy plane is directed towards axis 3 on which the cation is situated, then depending on the rotation of the latter, the shortest distances vary over the ranges: $O_{II} \cdots C = 2.40-2.67$; $O_{II} \cdots H = 1.34-2.00$ Å. The second is inadmissibly small. Consequently, such a relative disposition is impossible; the $Cl-O_{II}$ bond cannot be directed towards the upper anion. Thus, the relative displacement of the column along the z axis (1/3 or 2/3) is determined by the direction of the tilted Cl-O bonds; columns towards which these bonds point must be displaced by +1/3 relative to the given one.

In the second variant of the relative disposition of the cation and upper anion (the bisector of the angle between projections of $Cl-O_{II}$ and $Cl-O_I$ bonds on the plane xy is directed towards the cation) the shortest intermolecular distances vary over the ranges: $O_{II} \cdots C = 3.22-3.91$; $O_{II} \cdots H = 2.14-2.32$; $Cl \cdots H = 2.95-3.41$ Å. The first and last distances are normal; on the other hand, the second distance is considerably shortened. If this is ignored, the average intermolecular radii for the given structure are as follows: $R_C = 1.77 \pm 0.02$; $R_H = 1.22 \pm 0.05$; $R_O = 1.44 \pm 0.03$; $R_{Cl} = 1.80$ Å. Consequently, depending on the rotation of the cation, this shortening would be $R_O + R_H - (2.14 - 2.32) = 0.34 - 0.52$ Å. It is this shortening (of which there are six per anion and cation) which leads to compression of the anion perpendicular to axis 3, leading to the approach of O_{II} atoms to axis 3 with a substantial distortion of the valence angles. Thus, shortening of the intermolecular distance by ~ 0.4 Å is compensated by deformation of the valence angle by $15-20^\circ$, which agrees with other analogous cases of organic crystallochemistry [5]. If the intermolecular distance $O_{II} \cdots H$ were normal (3.66 Å), then with the same cell parameters, the valence angles would be deformed to an inadmissible extent and, on the other hand, with the normal valence angles of $109^\circ 28'$, the $O_{II} \cdots H$ distance would be inadmissibly shortened.

The reason for these distortions of the valence angles and shortening of the distances is the tendency towards dense packing. Actually, if a hypothetical structure, completely analogous to the real one, but with normal angles and distances were produced, its packing coefficient would be inadmissibly small ($k = 0.48$), while with the real structure $k = 0.72$, i.e., it has a normal value.

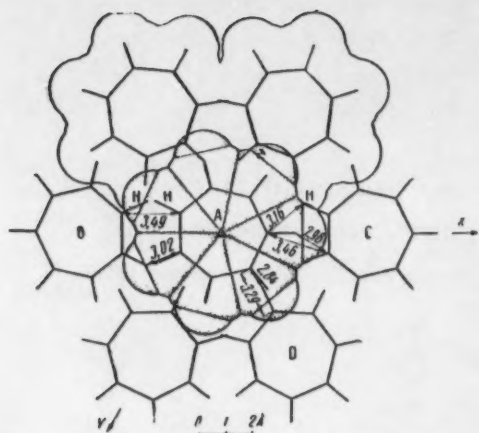


Fig. 5. Cation-cation contacts in the tropylium iodide structure.

The structure is built up of analogous columns $C_7H_7^+I^-C_7H_7^+I^-...$ (Fig. 3), in which the anion is arranged exactly in the middle between two cations. However, in this structure there is no contact in the columns and the dense packing is produced by the moving of the ions of the six neighboring columns into the "grooves" of the given column. The coordination number of the cation is 12 (3 cations above and 3 below, 3 anions above and 3 below) (Figs. 4 and 5). An anion touches six cations (3 above and 3 below). Depending on the rotation of the cations, the shortest intermolecular distances vary over the following ranges: $C---C=3.29-3.49$; $C---H=2.84-3.16$; $C---I=3.77-3.99$; $H---I=2.79-3.26$ Å. By taking the average values, we find the following intermolecular radii: $R_C=1.77 \pm 0.07$, $R_H=1.07 \pm 0.23$, $R_I=1.95 \pm 0.23$ Å. The wide ranges of variation of R_H and R_I are caused by the shortened $I---H$ distances. These shortenings (Fig. 4) cannot be eliminated by rotation of the cations; due

to the spherical nature of the anion, when they disappear in one place they appear in another. However, the number of short distances per anion-cation pair is small and considerably less than the number of normal contacts. In addition, these shortenings may be uniformly distributed throughout the structure, the packing coefficient of which has the high value $k=0.78$. For an analogous hypothetical structure with contacts at normal distances $k=0.64$, i.e., appreciably less. Thus, in this structure also the reason for the shortening of intermolecular distances is the tendency toward the creation of denser packing.

As has already been stated, the series of interatomic vectors leads to the arrangement of the anion at equal distances from two cations, present on the same axis 3, i.e., a centrosymmetrical structure, which contradicts the observed piezo effect, though it is true that this is weak. The reason for this contradiction is apparently the error in the determination of the z coordinates of the carbon atoms, which may reach 0.05 Å. If this is so, then the cation approaches one (for example, the upper) anion and moves away from the other, which eliminates the center of symmetry. It is also possible that, under the action of the crystal field, the symmetry of the tropylium ion is destroyed in the sense that its "upper" and "lower" sides become nonequivalent and this also eliminates the center of symmetry.

Both structures examined are characterized by the presence of remote order with the absence of close order. It is logical to speak of a gaseous-crystalline state of such objects, which include camphor, methane, hexachloroethane, quinuclidine, and some other solids, whose molecules acquire the statistical symmetry of rotating bodies in a crystal. The results of investigation of such crystals naturally cannot give exhaustive information on the molecular structure. Nonetheless, the present work makes it possible to determine quite accurately the radius of the tropylium nucleus "rotating in its own plane" (1.69 ± 0.03 Å) and showed that its deviations from coplanarity cannot exceed 0.1 Å. Both structures investigated were found to be purely ionic in their geometry.

SUMMARY

1. An x-ray structural investigation was made of the structure of tropylium perchlorate and iodide monocrystals by means of three-dimensional electron density series.
2. In both structures the tropylium ion occupied a statistically disordered position in the crystal, i.e., it "rotated" about an axis perpendicular to the plane of the ring. The radius of the ring was measured and the C—C bond length calculated as 1.47 Å.
3. The packing of molecules in the crystals was analyzed. The distortion of the form of the perchlorate ion is due to intermolecular forces, tending to arrange the molecules with maximum density.
4. Though there are in general no doubts about the ionic nature of the structures, attention should be paid to the polarity of the tropylium iodide crystal, which may indicate the presence of a weak exchange bond between the ring and the iodine ion.

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COMBUSTION OF GASOLINE-AIR MIXTURES IN TURBULENT FLOW

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Translated from *Izvestiya Akademii Nauk SSSR, Otdeleniye*

Khimicheskikh Nauk 1960, No. 1, pp. 45-52, January, 1960

Original article submitted June 6, 1958

The effect of turbulence on the rate of flame propagation was known as early as the last century. On the basis of Malyar and Le Chatelier's experiment and his own observations, Mikhel'son [1] stated that vortical and oscillatory movements of the flow greatly increased the ignition rate of the fuel mixture. In their work, Damkahler [2] and Shchelkin [3] presented relations of turbulent flame propagation velocity based on physical concepts of flame transfer by flow pulses u' and the normal flame velocity u_n . This scheme, based on physical concepts of flame propagation in turbulent flow has been used widely in a number of subsequent theoretical and experimental works [4-9] as the most widely accepted theory of turbulent flame propagation. Later Summerfield [10] and Shchetinkov [11] proposed a new physical model for flame transfer in turbulent flow, in which the basic assumption was that combustion in turbulent flow occurs in the volume rather than at the surface of the bent flame. The physical concepts of flame transfer in turbulent flow according to the Damkahler-Shchelkin scheme have been rejected in recent work.

It seems to us that there is no basis for rejecting the Damkahler-Shchelkin theory, though it requires some refinement. The flow pulsations involved in flame transfer require more accurate evaluation. On comparing these pulsations with the mean square pulsations u' of the incident flow, we find that the experimental data differ considerably from calculations according to the theoretical relation of Damkahler [2] and Shchelkin [3]. In his work, Karlovitz [6] showed that as the fuel mixture passes through the bent flame front, due to an increase in the specific gas volumes, energy is evolved during combustion and part of this increased the pulsations of the incident flow to a magnitude u'' . If the pulsations generated by the flame are taken into account, this should decrease the divergence between experimental data and results calculated by the Damkahler-Shchelkin theory [2, 3].

It should be noted that the present confusion in explanations of the mechanism of flame transfer by flow pulsations may lead to a considerable divergence between experimental data and theory. In addition, different explanations of this mechanism make it impossible to compare the experimental results of different authors. For example, on the basis of correct concepts of the effect of flow pulsations on the bending of the flame front, Karlovitz [6] and a number of foreign authors, using a burner method, evaluated the turbulent flame velocity at the surface passing through the line of maximum flame luminescence. However, both starting mixture and combustion products pass through this surface and the volume and velocity of the latter cannot be determined. With this treatment of the experimental material, the experimental data will be low.

Zel'dovich [12] showed that the rate of flame propagation in pipes is determined by the maximum velocity of the seat of the flame relative to the starting mixture. This approach could be applied to flame transfer in turbulent flow, considering that turbulent flame propagation rate would be the maximum velocity of projecting flame seats, relative to the starting mixture. This velocity should be evaluated from the gas throughput per unit of smooth surface passing through the peaks of the flame seats, projecting toward the fresh gas. It can be assumed that a more detailed calculation of the effective factors inherent in either method of investigation and a correct

TABLE 1

Turbulator	$\epsilon = u' / V_{av} \cdot 100\%$		
	glow discharge	thermoanemometer	average value
Grid	1.7	—	1.7
2 mm	4.0	—	4.0
Smooth	5.0	5.05	5.0
5 mm	8.5	7.4	8.0
8 mm	15.7	14.2	15.0

TABLE 2

α	0,5	0,6	0,7	0,8	0,9	1,0	1,1
u_{Π}	15	19	29	32	29	25	21
π	8,0	9,0	9,2	9,3	9,0	8,3	7,4

TABLE 3

$t, ^\circ\text{C}$	25	52	75	100	150	175	200
u_{Π}	30	33	37	40	49	55	60
π	9	8,3	7,8	7,3	6,5	5,8	5,3

TABLE 4

u' / u_{Π}	0,5	1,0	2,0	3,0	4,0	5,0	10	15	20	30
u_T / u_{Π}	3,21	4,4	6,57	8,28	9,8	11,2	17,2	22,3	26,7	34,8
k_1	4,4	3,4	2,7	2,35	2,1	2,0	1,6	1,37	1,25	1,09
k_2	0,8	0,98	1,17	1,23	1,27	1,28	1,25	1,18	1,12	1,02

explanation of the mechanism of turbulent flame transfer in treating experimental results should lead to an unequivocal relation for the turbulent flame propagation rate regardless of the experimental procedure used.

EXPERIMENTAL

In the study of flame propagation in a flow, the burner method is usually used and either the right or inverse cone of the flame studied. While this method is convenient for studying laminar flame, it is unsatisfactory for studying turbulent flames. The combustion zone may be determined with a high degree of error by the burner method and direct photography. By the use of Toepler's method for photographing the cone of a turbulent flame, only the outer contour of the combustion zone can be determined, while the contour of the inner surface of the flame cone cannot be determined at all. Since we consider that the main determining parameter for evaluating the turbulent velocity is the boundary between the starting mixture and the start of the combustion zone, we investigated the outer and inner contours of the combustion zone and photographed them by the Toepler method, using an optical burner.

The burner had a square cross section of 40×40 mm and its two opposite walls were shortened to 40 mm and were continued by two optical quartz plates, 140×240 mm. As shown in Fig. 1, by adding two more plates it was possible to photograph flames up to 480 mm long by the Toepler method. The two projecting walls of the burner between the quartz plates had a device for the admission of auxiliary fuel mixture (hydrogen), which

served as a stabilizing source for igniting the starting mixture. Various devices for changing the turbulent characteristics of the flow were arranged 55 mm from the mouth of the burner; these were a grid with 625 openings per cm^2 , a row of wires 2 mm in diameter, a smooth, square tube, 40×40 mm, 50 diameters in length, without turbulators, a row of wires 5 mm in diameter and a row of wires 8 mm in diameter. The wires were spaced two diameters apart, parallel to the line of the operating ignition source of the mixture. The values of the extent of turbulence of the incident flow, given in Table 1, were measured with an anemometer with a glow discharge and a thermoanemometer, 135 mm from the turbulators along the axis of the flow.

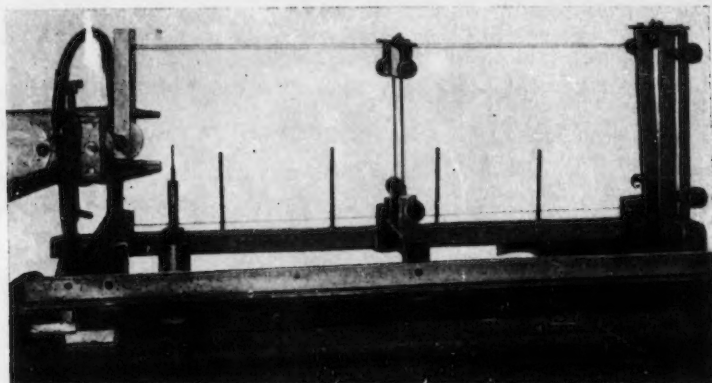


Fig. 1. Photograph of an optical burner with quartz windows.

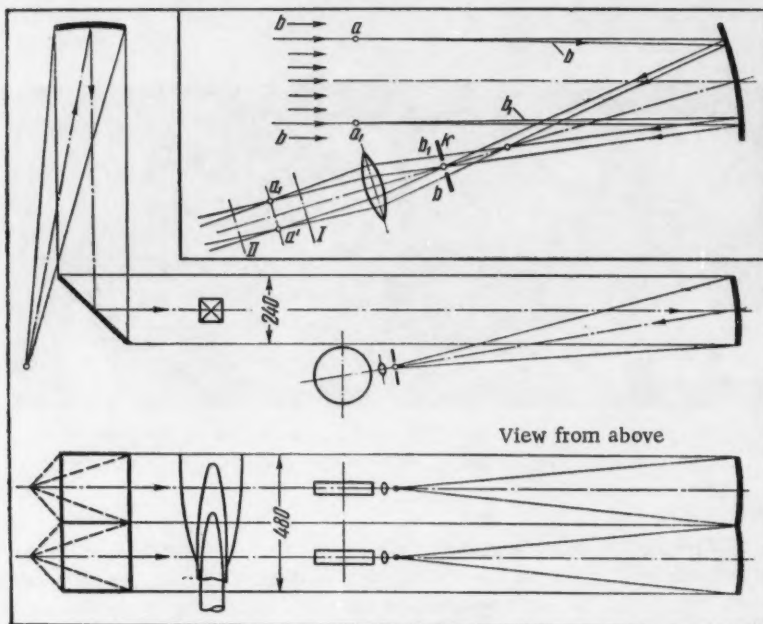


Fig. 2. Optical scheme for photographing flames by Toepler's method. Size of parallel beam 240×480 mm.

The turbulence generated by the flame was evaluated mainly by Karlovitz's method [6] and we considered that under the action of the flow pulsations on the flat front of the flame, the bent surface formed a right cone, whereby regardless of the magnitude of the pulsating mole and the size of the ratio $\frac{u^*}{u_n} \geq 1$, the surface of the cone would be greater than its base by the value

$$\frac{S_0}{S_{\text{base}}} = \frac{1}{\cos \alpha} = \frac{u_n + u'}{u_n}, \quad (1)$$

where α is the angle between the cone formed and a radius of its base. As the fuel mixture passes through the flame front, due to the increase in the specific gas volume, there is evolution of energy, which is proportional to the square of the increase in the velocity $\left[\frac{V_2 - V_1}{V_1} \cdot u_n \right]^2$ and is directed along the normal to the flame surface.

In the case of a flat flame front, the vector of the increase in velocity coincides with the direction of flame propagation and the energy from the increase in specific gas volume is consumed in creating a fall in pressure between the starting mixture and the combustion products. When a flame front of a regular conical type is bent, the vector of the velocity increase will differ from the propagation vector of the turbulent flame by the angle α , whose cosine is equal to $\cos \alpha = \frac{u_n}{u' + u_n}$. In this case part of the energy evolved, proportional to $\left[\frac{V_2 - V_1}{V_1} u_n \cos \alpha \right]^2$ will be consumed in creating a fall in pressure between the starting mixture and the combustion products, while the rest of the energy will be consumed in further turbulence of the flow. For a three-dimensional energy distribution and isotropic turbulence Karlovitz [6] gave the following relation

$$3u''^2 = \left[\frac{V_2 - V_1}{V_1} \cdot u_n \right]^2 - \left[\frac{V_2 - V_1}{V_1} \cdot u_n \cdot \cos \alpha \right]^2 \quad (2)$$

On writing $\frac{V_2 - V_1}{V_1} = \pi - 1$, we obtain

$$u'' = \frac{\pi - 1}{\sqrt{3}} u_n [1 - \cos^2 \alpha]^{0.5} \quad (3)$$

where u'' is the pulsation generated by the flame.

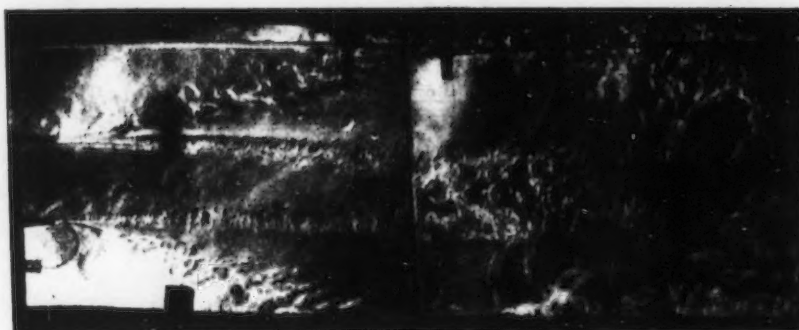


Fig. 3. Photograph of a gasoline-air mixture flame, obtained by Toepler's method (one of the frames from a series of 15). The degree of turbulence $\epsilon = 1.7\%$.

In determining u'' from Eq. (3) for the evaluation of $\cos \alpha$, in the first approximation we took the mean square value of the flow pulsation. At low values of the flow pulsations, $u' < 0.5 u_n$, a considerable deviation of the bent flame surface from a conical shape is possible and this could result in greater errors in the determination of u'' . At values of $u'/u_n > 5$, the pulsation generated by the flame reaches its maximum value, $u'' = \frac{\pi - 1}{\sqrt{3}} \cdot u_n$.

The increase in the specific gas volume π during combustion was determined in an investigation of the relation between the normal flame velocity in gasoline-air mixtures and the gas composition and temperature.* The average values of u_n and π obtained with an initial temperature of the gasoline-air mixture of 20° are given

* These experiments were carried out by Yu. A. Bokhon.

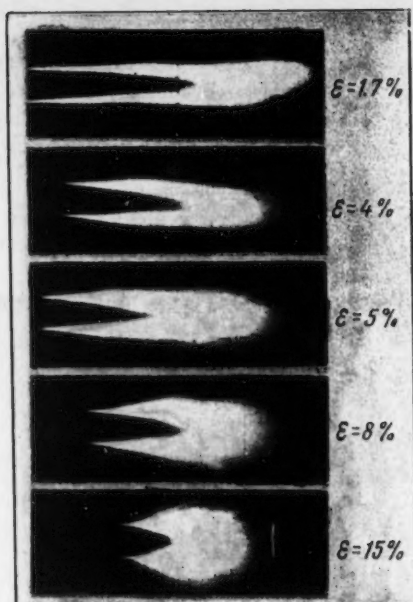


Fig. 4. Effect of degree of turbulence on the flame form. Direct photographing of flame at a constant flow rate $v = 33$ m/sec, an air excess $\alpha = 0.85-0.89$, and a degree of flow turbulence $\epsilon = 1.7-15\%$.

in Table 2. The values of u_n and π at $\alpha = 0.9$ in relation to the mixture temperature are given in Table 3. In determining u'' , we used the values for u_n and π from Tables 2 and 3 with allowance for the experimental conditions.

The optical arrangement for photographing the flame by Toepler's method is shown in Fig. 2. The considerable heat inhomogeneity gradients in the combustion zone made it possible to use a simplified Toepler scheme, which consisted of two matched spherical mirrors, 240×240 mm, with a spherical radius $R = 2400$ mm. The matched equipment made it possible to photograph flames 240×480 mm by Toepler's method. Instead of blades, 1.2 mm openings (near the light source) and a screen of the same dimensions (near the photorecorder) were arranged at the focuses of the mirrors. A lens for focusing the burner (jet) onto the film was placed between the screen and the film of the photorecorder. As the ray passed through the heat inhomogeneities, it passed beyond the limits of the screen and illuminated the film, thus fixing the position of the combustion zone. The light source was a condensed discharge in a capillary filled with hydrogen. By using Neubert's circuit [13] and a discharger of our own design, we obtained a serial discharge with a frequency of up to 150,000 cps. Individual frames showed the possibility of arranging a serial discharge with a frequency of up to 500,000 cps. In the experiments we used a serial discharge with a frequency of 1500 cps, and obtained ~ 15 frames of successive photographs of flames. Fig. 3 shows a photograph of the flame of a burning gasoline-air mixture at a flow turbulence of $\epsilon = 1.7\%$.

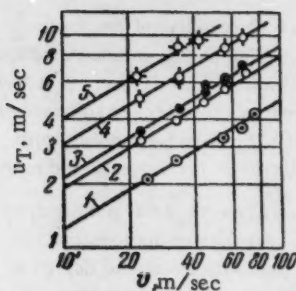


Fig. 5. Set of curves for the turbulent flame velocity u_T in relation to flow velocity v and degree of turbulence: 1) $\epsilon = 1.7\%$; 2) $\epsilon = 4\%$; 3) $\epsilon = 5\%$; 4) $\epsilon = 8\%$; 5) $\epsilon = 15\%$.

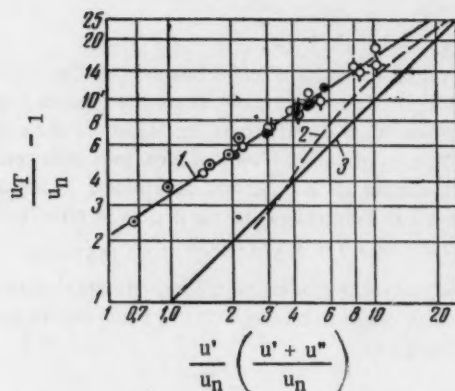


Fig. 6. Dimensionless turbulent flame velocity u_T/u_n in relation to dimensionless pulsation u'/u_n : curve 1) $(u_T/u_n) - 1 = f(u'/u_n)$; curve 2) $(u_T/u_n) - 1 = f(u' + u'')/u_n$; curve 3) $(u_T/u_n) - 1 = (u' + u'')/u_n$.

The turbulent velocity of the flame \underline{u} was evaluated at the internal smooth surface passing through the flame seats projecting to the greatest extent towards the fresh gas. It should be noted that the results of measuring the turbulent velocity of the flame \underline{u} in a series varied over the range of $\pm 6\%$ of the average value. This scatter may be explained by the effect of separate projections of flame seats caused by pulsations considerably exceeding the average value in the pulsation spectrum. The application of Toepler's method made it possible to determine accurately the limits of the internal and external combustion zones formed and thus the value of \underline{u} also.

Simultaneously with serial photography by Toepler's method, we used direct photography with an exposure time of $5 \mu\text{sec}$. A series of photographs taken by direct photography with a constant temperature and a flow rate of $v = 33 \text{ m/sec}$, but with a varying degree of turbulence is shown in Fig. 4. These photographs may serve as a qualitative explanation of the phenomenon investigated, but the quantitative values are determined from the serial photographs.

The main series of experiments was carried out with a constant air excess ($\alpha \approx 0.8$), a flow rate at the burner outlet of $v = 22-76 \text{ m/sec}$, a gasoline-air mixture temperature $T = 440 - 470^\circ \text{K}$, and a degree of flow turbulence $\epsilon = 1.7 - 15.0\%$.

The results of a series of experiments carried out at constant turbulence and at approximately constant temperature and air excess are described well by the following relation:

$$u_T = k v^{0.6} \quad (4)$$

For a whole series of experiments with the degree of turbulence varying over the range $\epsilon = 1.7-15\%$, we obtained a set of curves (Fig. 5) where the greater degree of turbulence corresponds to the greater value of u_T . The set of curves is described by Eq. (4) where the coefficient k is a function of the degree of turbulence, $k = f(\epsilon)$. The set of curves obtained show that with combustion in different burners or furnaces the flow rate and Reynold's number are not general parameters in the investigation of turbulent flame velocity. The relation of coefficient k in Formula (4) to the degree of turbulence ϵ shows that such a general parameter is the pulsation component of the flow, which equals $u' = \frac{\epsilon \cdot v}{100}$.

The results of processing the experimental data are given in Fig. 6. Curve 1, where the pulsation component of the flow is taken to be equal to the mean square pulsation of the incident flow, is described by a relation of the following form:

$$\frac{u_T}{u_n} = 1 + 3.4 \left(\frac{u'}{u_n} \right)^{1/5} \quad (5)$$

or

$$\frac{u_T}{u_n} = 1 + k_1 \frac{u'}{u_n}, \quad (6)$$

where

$$k_1 = 3.4 \left(\frac{u_n}{u'} \right)^{1/5} \quad (7)$$

The theoretical equation for the turbulent flame velocity, taking into account the turbulence generated by the flame, has the following form:

$$\frac{u_T}{u_n} = 1 + \frac{u'}{u_n} + \frac{u''}{u_n} \quad (8)$$

or in the full form

$$\frac{u_T}{u_n} = 1 + \frac{u'}{u_n} + \frac{\pi - 1}{\sqrt{3}} \left[1 - \left(\frac{u_n}{u_n + u'} \right)^2 \right]^{0.5} \quad (9)$$

In Fig. 6, curve 2, shown by dashes, corresponds to the average values of the experimental data with allowance for the turbulence generated by the flame. Curve 3 is plotted from theoretical Eq. (8). On examining curves 2 and 3 one can see that when turbulence generated by the flame is taken into account, the experimental data are much closer to the theoretical ones. In this case the theoretical value for the over-all pulsations $u'/u_n + u''/u_n$ is less than the pulsations involved in flame transfer found experimentally by the value k_2 .

Table 4 gives the experimental values for turbulent flame velocity u_T/u_n calculated from Eq. (5) and the values of the coefficients k_1 and k_2 .

The high correction factors k_1 , especially in the range $u'/u_n \approx 1$, where the pulsations involved in flame transfer are 3 to 4 times greater than the pulsations measured in the incident flow, were the basis for assertions that the theory of flame transfer at a normal velocity and by the flow pulsations is not confirmed experimentally. When turbulence generated by the flame, u''/u_n , is taken into account, the over-all value of the pulsations, $u'/u_n + u''/u_n$, agrees with experiment with an accuracy of up to the coefficient k_2 , i.e., up to 28% of the maximum deviation. The experimental equation (8) differs from the theoretical equation (8) by the value k_2 and appears as follows:

$$\frac{u_T}{u_n} = 1 + k_2 \left[\frac{u'}{u_n} + \frac{u''}{u_n} \right], \quad (10)$$

where k_2 is taken from Table 4.

The turbulence generated by the flame at $u'/u_n > 5$ reaches a limiting constant value $u''/u_n = \frac{\pi-1}{\sqrt{3}}$. For a gasoline-air mixture; $\alpha = 0.8$; $T = 450^\circ\text{K}$; $\pi = 5.8$; $\frac{u'}{u_n} > 5$; the turbulent flame velocity equals:

$$u_T = u_n + k_2 [u' + 2.8 u_n]. \quad (11)$$

These experiments were carried out under gasoline-air mixture combustion conditions close to $\alpha = 0.8$ and approximately constant normal flame velocity. In the future we plan to carry out experiments under conditions of widely different normal flame velocities, temperature, and pressure in measuring the average value of the pulsations in the incident flow which affect the foremost flame front.

SUMMARY

1. When the total turbulence of the isothermal incident flow and that generated by the flame are taken into account, the experimental data are quite close to the theoretical, thus confirming the physical concepts put forward by Damkahler and Shchelkin on flame transfer in turbulent flow by the flow pulsations and normal flame velocity.
2. The direct dependence of the turbulence generated by the flame on the normal combustion velocity increases the value of the latter in the transfer of flames in turbulent flow.
3. The turbulent flame propagation rate is determined by the maximum velocity of the flame seats relative to the fuel mixture.
4. The seats projecting towards the fresh fuel mixture form the foremost front of the flames and from these, as ignition sources, burn-up of the mixture proceeds in the combustion zone at the pulsation-bent flame surface.

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POSSIBILITY OF THE FORMATION OF A HYDROGEN BOND
BETWEEN A PEROXIDE RADICAL AND MOLECULES
WITH HYDROXYL GROUPS

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Translated from *Izvestiya Akademii Nauk SSSR, Otdelenie
Khimicheskikh Nauk* 1960, No. 1, pp. 53-58, January, 1960
Original article submitted March 31, 1958

Many radical and chain reactions involve free atoms and radicals of high reactivity. The high reactivity of free radicals is connected with the presence of one unpaired electron in them. At the present time two types of reaction between free radicals and molecules are known [1]. Free radicals readily undergo an addition reaction with molecules which have multiple bonds. For example, in the oxidation of hydrocarbons the following reaction occurs: $R + O=O \rightarrow ROO$.

The other type of reaction is an exchange reaction, for example



In both types of reactions there is rupture of some and formation of other chemical bonds. Yet another type of chemical interaction between a free radical and certain molecules is possible, namely the formation of a chemical bond without the rupture of bonds in the molecule, i.e., complex formation. The possibility of complex formation between a free radical and a molecule of a definite chemical compound follows logically from the existence of intermolecular complexes and the chemical unsaturation of free radicals. While electrostatic attraction forces play a great part in the formation of complexes between oppositely charged ions and between ions and polar molecules, the main role in the formation of intermolecular complexes is played by the donor-acceptor interaction of the electron shells of the two molecules forming the intermolecular bond [2]. At the present time, many examples are known of chemical interaction between valence-saturated molecules. This fact and the presence of one unpaired electron in free radicals indicates a real possibility of chemical interaction between certain molecules and free radicals. The most favorable possibilities for such an interaction between molecules and free radicals exist in the liquid phase.

A widespread case of chemical interaction between molecules is the formation of an intermolecular hydrogen bond. In bifunctional organic compounds there is the possibility of the formation of an intramolecular hydrogen bond. A molecular hydrogen bond is also formed by such hydroxyl-containing substances as water, alcohols, and acids. Precisely these substances are formed during the liquid-phase oxidation of organic substances by molecular oxygen, which involves peroxide free radicals. The presence of peroxide free radicals and also hydroxyl-containing molecules, which tend to form a molecular hydrogen bond, in the oxidation system naturally raises the question of the possibility of chemical interaction between them with the formation of a free radical hydrogen bond $ROO \cdots HOX$, where X may be H, R, RCO, and RO. The molecular hydrogen bond $O-H \cdots O$ is formed between a hydrogen atom and a valence-saturated O atom, present in water, hydroperoxide, alcohol, and acid. Although the H atom in hydroxyl bears a net positive charge and the oxygen atom bears a net negative charge, a molecular hydrogen bond is formed not so much due to the electrostatic attraction of these atoms as due to interaction of the oxygen atom electrons with the hydrogen atom [3]. Therefore one would expect that the presence of an unpaired electron

TABLE

Effect of Water on the Activity of Radicals in the Oxidation of Cyclohexanone

H ₂ O in %	v in mmole/liter· min	w in mmole/liter· min	v/√w
0	35	0.91	37
1.9	8.7	0.63	11
3.8	10.3	0.88	11
6.2	6.5	0.52	9
9.4	5	0.36	8.3

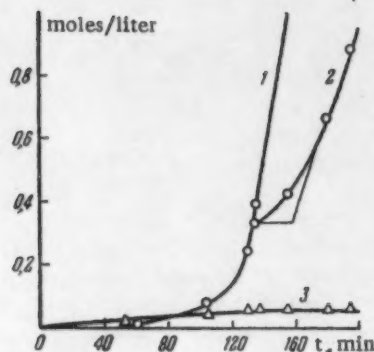


Fig. 1. Oxidation of cyclohexanone at 120° and 10 atm; 1) kinetic curve of acid formation; 2) kinetic curve of acid formation after introduction of inhibitor; 3) kinetic curve of hydroperoxide accumulation.

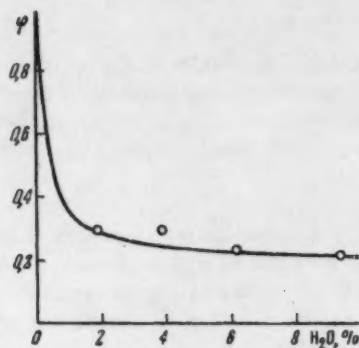


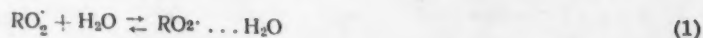
Fig. 2. Decrease in the rate of chain propagation in the presence of water. The points represent experimental data. The curve was calculated from the

$$\text{formula } \varphi = \frac{1 + 0.8 [\text{H}_2\text{O}]}{1 + 4 [\text{H}_2\text{O}]}$$

in the peroxide radical would lead to the formation of the bond $\text{ROO} \cdots \text{HOX}$, which is stronger than the molecular hydrogen bond $\text{O} \cdots \text{HOX}$. Thus, the formation of a radical hydrogen bond is quite possible theoretically. The essential difference between such a radical hydrogen bond and a molecular bond would be as follows. The molecular hydrogen bond is formed as a result of interaction of the electrons of a valence-saturated oxygen atom with a hydrogen atom. The radical hydrogen bond would be formed mainly as a result of interaction between the hydrogen atom and the unpaired electron present in the free peroxide radical. A radical hydrogen bond may be formed both between the free radical and a molecule and within the free radical if it contains a hydroxyl group and interaction between the $\text{O}-\text{O}^{\bullet}$ and $\text{O}-\text{H}$ groups is geometrically possible.

The direct experimental detection of a radical hydrogen bond encounters enormous experimental difficulties connected with the extremely low concentration of peroxide radicals in an oxidation reaction. This circumstance compels us to look for other, indirect methods of detecting a radical hydrogen bond. As was shown in the work of Émanuél' and his co-workers [4], under certain conditions a molecular hydrogen bond may manifest itself kinetically. Therefore it is natural to expect that a radical hydrogen bond may also be detected kinetically in a suitably devised experiment.

The rate of an oxidation reaction is determined by the concentration and reactivity of the free radicals. In the presence of a substance with a hydroxyl group, for example, water, there should occur the formation of radical-complexes by the reversible reaction

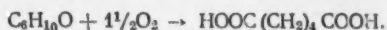


In the radical-complex formed, the free valence is to some extent saturated due to the chemical bond with

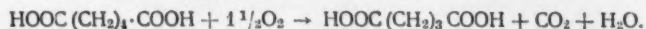
the molecule and therefore the radical-complex must be less active than the free peroxide radical. Consequently, in the presence of water some of the peroxide radicals are converted into less active radical-complexes and this should decrease the rate of chain propagation. A decrease in the chain propagation rate in a complex chain reaction may be detected in the following way: An oxidation may be carried out with the free radicals produced at a constant rate in experiments without a hydroxyl-containing substance and with such a substance introduced and the reaction rate measured. Another method consists of determining the oxidation rate v in a developed oxidation reaction and also, by an inhibition method, the chain initiation rate, w . Since $v = k [RH]n$, and with second order chain termination in a liquid-phase reaction, the concentration of free radicals $n \sim \sqrt{w}$, then the value v/\sqrt{w} will characterize the rate of chain propagation (or the total activity of the free radicals in the reaction). By carrying out experiments without a hydroxylic substance and with the addition of such a substance to the oxidation system, it is possible to establish whether the total activity of the radicals changes from this or remains unchanged. The latter method was used in the present work.

In choosing a substance capable of forming a hydrogen bond with a peroxide radical it is necessary to consider the following. The total activity of the radicals in the reaction may decrease not only due to the formation of radical complexes, but also as a result of the reaction of radicals with molecules of the substance introduced and the change in composition of the radicals resulting from such a reaction [5]. Therefore, for kinetic detection of the hydrogen bond and an unequivocal interpretation of the results obtained it is necessary to take a substance which is incapable of undergoing an exchange reaction with the ROO^{\cdot} radical. For precisely these reasons it is impossible to take such substances as alcohols, acids, and hydroperoxides, as peroxide radicals will react with them to change the composition of the radicals and an unequivocal interpretation of the results obtained will be impossible. The most suitable substance for the detection of a radical hydrogen bond is water. The O-H bond in a water molecule is very strong (bond energy 118 kcal/mole). For the rupture of this bond by the peroxide radical, the very great activation energy of 32 kcal/mole must be overcome. Therefore the introduction of water into the reaction mixture hardly changes the composition of the radicals. In addition, even if it is assumed that there is partial replacement of peroxide radicals by hydroxyls, this can only accelerate chain propagation as hydroxyl radicals are much more active than peroxide radicals. Thus, a decrease in the rate of chain propagation in an oxidation reaction after the introduction of water can only be the result of the formation of radical complexes through a radical hydrogen bond.

Hydrocarbons are unsuitable for use as the substance oxidized, as they are practically immiscible with water. Alcohols themselves are capable of forming a hydrogen bond and this could completely eliminate the effect of water. Therefore, cyclohexanone, which is readily oxidized, was chosen as the substance for oxidation. Cyclohexanone dissolves a considerable amount of water and is oxidized at quite a low temperature. It is also very important that very little water is formed as a result of its oxidation. The main course of the oxidation of cyclohexanone, namely the formation of adipic acid, proceeds without the formation of water:



During the course of the reaction, adipic acid gradually undergoes oxidative decarboxylation:



The molecular intermediate products in the oxidation of cyclohexanone are an α -ketohydroperoxide and the half aldehyde from adipic acid [6].

EXPERIMENTAL

Experiments to determine the effect of water on the chain propagation rate were carried out in the following way. Freshly distilled cyclohexanone (160 ml) either without water or with a few volume percent of water added was oxidized at 120° with a mixture of nitrogen and oxygen in a ratio of 1 : 1, passed at a rate of 30 liter/hr, in an autoclave at 10 atm fitted with a stirrer. During the experiment samples of the oxidized cyclohexanone were taken and analyzed for hydroperoxide (iodometrically) and acid content. The inhibitor, α -naphthol, was introduced into the developed reaction. The inhibitor concentration at the moment of introduction into the reaction zone was 11 mmole/liter. The reaction retardation period due to the α -naphthol introduced, t_{in} , was determined

from the change in the kinetic curve of acid accumulation after introduction of the inhibitor. As one inhibitor molecule normally terminates two chains, the rate of chain initiation at the moment of inhibitor introduction

$$w = \frac{2[\text{InH}]}{t_{\text{in}}} = \frac{22}{t_{\text{in}}} \text{ mmole/liter} \cdot \text{min.}$$

The rate of acid formation, v , at the moment of inhibitor introduction

was found from the kinetic curve of acid formation. Figure 1 shows kinetic curves of hydroperoxide and acid accumulation during the oxidation of cyclohexanone before and after introduction of the inhibitor. This figure shows that the inhibitor did not stop the reaction completely, but only slowed it for a certain period of time. This was connected with the very high rate of chain initiation. Lines in Fig. 1 show how the time interval t_{in} was found. In the physical sense, this is the time interval after which the inhibitor would disappear completely if all the free radicals reacted only with inhibitor molecules. The table gives results obtained in the present experiments.

As the table shows, the introduction of water considerably reduced the over-all activity of the radicals, characterized by the value v/\sqrt{w} . Thus, the experimental results obtained qualitatively confirm the hypothesis on the formation of a radical hydrogen bond and its kinetic manifestation.

Let us examine the problem of the quantitative relation between the over-all activity of the radicals and the concentration of water introduced. In the presence of water (or some other hydroxylic substance), as a result of the equilibrium reaction (1), some of the ROO^\cdot radicals are converted into radical-complexes $\text{ROO}^\cdot \dots \text{H}_2\text{O}$. These complexes are free radicals which are less active than ROO^\cdot radicals, but, generally speaking, are capable of participating in the chain propagation reaction. Let us denote the rate constant of the chain propagation reaction for radical-complexes as k' . Consequently, in the presence of water with the formation of radical-complexes, for the rate of the chain oxidation reaction we should write the equation:

$$v = -\frac{d[\text{RH}]}{dt} = k[\text{RH}][\text{RO}_2^\cdot] + k'[\text{RH}][\text{RO}_2^\cdot \dots \text{H}_2\text{O}].$$

It can be assumed that the rate of free radical recombination does not change appreciably in the presence of radical-complexes. This assumption is very probable as recombination proceeds practically without an activation energy and does not depend on the activity of the free radicals. In this case we may write $n = \sqrt{\frac{w}{k_r}}$, where k_r is the rate constant of peroxide radical recombination and $n = [\text{RO}_2^\cdot] + [\text{RO}_2^\cdot \dots \text{H}_2\text{O}]$. As due to equilibrium (1), $[\text{RO}_2^\cdot \dots \text{H}_2\text{O}] = K[\text{H}_2\text{O}][\text{RO}_2^\cdot]$, where K is the equilibrium constant, then

$$[\text{RO}_2^\cdot] = \frac{n}{1 + K[\text{H}_2\text{O}]} \quad v = \left(\frac{k}{1 + K[\text{H}_2\text{O}]} + \frac{k'K[\text{H}_2\text{O}]}{1 + K[\text{H}_2\text{O}]} \right) [\text{RH}] \sqrt{\frac{w}{k_r}},$$

hence

$$\frac{v}{\sqrt{w}} = \frac{1 + \alpha[\text{H}_2\text{O}]}{1 + K[\text{H}_2\text{O}]} \cdot \text{const},$$

where

$$\alpha = \frac{k'}{k} K, \quad \text{const} = \frac{k[\text{RH}]}{\sqrt{k_r}}$$

and in the absence of water $\frac{v}{\sqrt{w}} = \text{const}.$

The change in the activity of the radicals as a result of the introduction of water may be characterized by the ratio:

$$\varphi = \left(\frac{v}{\sqrt{w}} \right)_{\text{H}_2\text{O}} : \left(\frac{v}{\sqrt{w}} \right) = \frac{1 + \alpha[\text{H}_2\text{O}]}{1 + K[\text{H}_2\text{O}]} \quad (2)$$

This formula shows that with an increase in the concentration of water, the value φ should decrease and tend to a limiting value, equal to $\frac{k'}{K}$. If the water concentration is low or the equilibrium displaced to the left (low value of K), then v/\sqrt{w} remains practically constant. As the formation of a radical hydrogen bond

proceeds with the liberation of energy, with a rise in temperature K will decrease and consequently the effect of the radical hydrogen bond on the reaction kinetics will decrease. At sufficiently high temperatures this effect will disappear completely.

In Fig. 2 the data obtained experimentally are compared with the theoretical curve constructed from Formula (2). The course of the theoretical curve agrees satisfactorily with the points obtained experimentally. Thus, a kinetic study of the effect of water on the activity of peroxide radicals in the oxidation of cyclohexanone leads to results which agree well with the hypothesis on the formation of a hydrogen bond between a peroxide radical and a water molecule.

The hypothesis on the formation of radical-complexes of the type $RO_2 \cdots HOR$, is of fundamental importance in the study of the kinetics of chain reactions in liquid-phase oxidation of organic compounds and, in particular, hydrocarbons. In the course of such a reaction various hydroxyl-containing products such as water, alcohols, and acids are formed and accumulate. By forming complexes with peroxide radicals, they retard the oxidation reaction. Consequently, the formation of a radical hydrogen bond is one of the possible reasons for the self-retardation of oxidation processes. If a radical hydrogen bond is formed between a peroxide radical and a molecule with a hydroxyl group, then the formation of an analogous bond is also quite possible for such radicals as alkoxyl, hydroxyl, phenoxyl, and the HO_2 radical.

The possibility of complex formation between free radicals and molecules can also be deduced theoretically from a somewhat different point of view. It is known that free radicals, as particles with a high chemical energy, tend to stabilize themselves with the evolution of energy. The stabilization of free radicals may be accomplished by various methods. If the free radical contains π -electrons of a double bond or a benzene ring, with which the electron of the free valence may interact, then "intraradical" stabilization of the free valence occurs. Complete saturation of the free valence is possible when two free radicals react together to form molecular products. The formation of a complex between a molecule and a free radical is also a method of stabilizing the free valence. In such a complex the chemical energy of the unpaired electron is to some extent consumed in the formation of the bond in the complex and this also leads to partial stabilization of the free valence. Since a molecule participates in such complex formation, there is the possibility of a specific effect of this or that solvent on the reactivity of the given free radical. It is very probable that the effect of a solvent on the rate of a chain or radical reaction in individual cases is connected with this form of complex formation.

SUMMARY

1. It was shown that there are grounds for considering the possibility of the formation of a radical hydrogen bond between a peroxide radical and molecules with hydroxyl groups. The formation of such bonds under the conditions of an oxidation reaction should decrease the rate of chain propagation.
2. By means of inhibition during the course of the reaction, on the example of cyclohexanone oxidation, it was established experimentally that water has a retarding action on chain propagation and this confirms the formation of a hydrogen radical bond in this system.

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EXCHANGE REACTIONS OF CHELATE IRON COMPOUNDS

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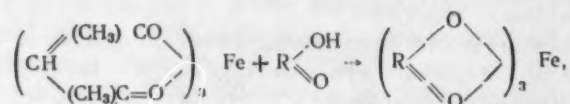
Translated from *Izvestiya Akademii Nauk SSSR, Otdelenie*

Khimicheskikh Nauk No. 1, pp. 59-62, January 1960

Original article submitted June 17, 1958

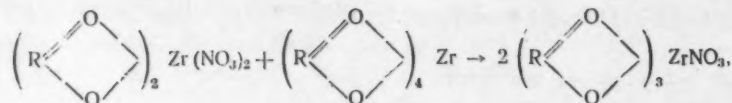
Studies of the exchange reactions of chelate compounds of metals have been confined to isolated cases. In previous communications [1-3] we showed that chelate zirconium compounds can undergo exchange reactions; we studied the exchange reactions of zirconium tetrakisacetylacetonate and of zirconium trisacetylacetonate chloride with benzoylacetone, salicylaldehyde, acetoacetic ester, and alcohols. We observed the exchange of acetylacetonate residues for other chelating groups or alkoxyls, even when this was associated with change in the coordination number of zirconium. There is a reference in the patent literature [4] to the formation of colored high-melting polymers in the fusion of acetylacetonates of bivalent metals with tetraketones and subsequent removal of acetylacetonate by distillation.

Exchange reactions of chelate iron compounds were investigated along lines analogous to those followed for chelate zirconium compounds. It was found that iron trisacetylacetonate undergoes double decomposition with benzoylacetone and with salicylaldehyde when heated with these substances in a vacuum:

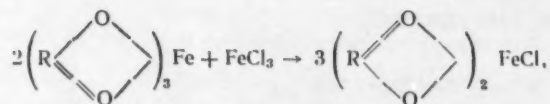


in which $\text{R} \begin{array}{c} \text{OH} \\ \diagup \quad \diagdown \\ \text{O} \end{array}$ is benzoylacetone or salicylaldehyde.

The reverse of disproportionation, which was carried out for chelate zirconium compounds by reaction of zirconium tetrakisacetylacetonate and of zirconium tetrakisbenzoylacetone with the corresponding dinitrates,

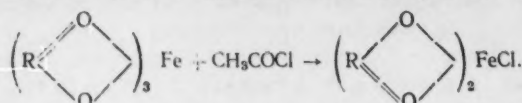


was found to be applicable also in the case of chelate iron compounds. Thus, heating of iron trisacetylacetonate and of iron trisbenzoylacetone with anhydrous ferric chloride in benzene gave the corresponding monochlorides:



in which $\text{R} \begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{O} \end{array}$ is an acetylacetonate or benzoylacetone residue.

The structure of the resulting monochlorides, which have not been described previously, was proved by their synthesis from iron trisacetylacetonate and trisbenzoylacetonate and acetyl chloride:



It is interesting that the acetylacetonate groups of iron bisacetonyle chloride are replaced by benzoylacetonate groups under the action of benzoylacetonate:



EXPERIMENTAL

The experiments were carried out with dry substances under conditions which excluded access of moisture.

Reaction of Iron Trisacetylacetonate with Benzoylacetonate

A solution of 1 g (0.0028 mole) of iron trisacetylacetonate in 2 ml of benzene was added to a benzene solution of 2.76 g (0.017 mole) of benzoylacetonate. At 50-55° under a residual pressure of 120-130 mm, acetylacetonate and benzene gradually distilled off. Addition of benzene with subsequent distillation of a mixture of benzene with the acetylacetonate liberated was repeated until the distillate gave a negative test for the presence of acetylacetonate with ferric chloride (ten hours). The solid residue obtained after removal of traces of solvent at 40° and 1 mm was carefully washed free from unchanged benzoylacetonate and iron trisacetylacetonate with hot ethanol and was washed with petroleum ether and dried on the filter for one hour in a stream of dry air. The crude product amounted to 1.3 g (85%). After recrystallization from benzene the substance melted* at 222-224°. The literature [5] gives m.p. 224°. Found: C 66.77; 66.92; H 5.09; 5.19; Fe 10.44; 10.54%. $(\text{C}_{10}\text{H}_9\text{O}_2)_2\text{Fe}$. Calculated: C 66.79; H 5.04; Fe 10.36%.

Reaction of Iron Trisacetylacetonate with Salicylaldehyde

Iron trisacetylacetonate (1 g) was dissolved in 20 ml of salicylaldehyde. Reaction was carried out with heating at a residual pressure of 40 mm. As acetylacetonate and excess of salicylaldehyde distilled over, further 15-ml portions of salicylaldehyde were added. In all, the reaction lasted 8-9 hours. The product was precipitated from benzene solution with petroleum ether, washed, and dried. Traces of salicylaldehyde and solvent were tenaciously held by the product, and with great difficulty it was freed from these by drying in an Abderhalden pistol at a residual pressure of 1 mm. The product amounted to 0.9 g (76%). After recrystallization from a mixture of benzene and petroleum ether the substance melted at 183-185°; melting was preceded by disintegration. Found: C 60.50; 60.25; H 3.87; 3.78; Fe 12.77; 12.98%. $(\text{C}_8\text{H}_7\text{O}_2)_3\text{Fe}$. Calculated: C 60.16; H 3.61; Fe 13.33%.

Reaction of Iron Trisacetylacetonate with Ferric Chloride

A solution of 0.48 g (0.0029 mole) of anhydrous ferric chloride in 1.50 ml of absolute ethanol was added to a solution of 2.06 g (0.0058 mole) of iron trisacetylacetonate in 7 ml of benzene. The reaction mixture was stirred at 40° for 3.5 hours. The solution was filtered, and solvent was distilled off; the crystalline residue amounted to 2.5 g. The product was purified by precipitation from benzene solution from petroleum ether and subsequent crystallization from benzene; when heated, it decomposed and then melted at 193-194°. Found: C 41.45; 41.39; H 4.84; 5.07; Fe 19.14; 19.46; Cl 12.08; 12.36%. $(\text{C}_5\text{H}_7\text{O}_2)_2\text{FeCl}$. Calculated: C 41.46; H 4.87; Fe 19.30; Cl 12.25%.

Iron bisacetylacetonate chloride is a hygroscopic dark-red crystalline substance; it is readily soluble in alcohol and chloroform, less soluble in benzene, sparingly soluble in diethyl ether, and insoluble in petroleum ether.

Reaction of Iron Trisacetylacetonate with Acetyl Chloride

A solution of 0.78g (0.01 mole) of acetyl chloride in 2 ml of benzene was added gradually with cooling to a solution of 3.53 g (0.01 mole) of iron trisacetylacetonate in 5 ml of benzene, and the mixture was then heated

*The melting points of this and other substances were determined in sealed capillaries.

for three hours at 85-90°. The crystals precipitated when the clear solution was cooled; they were filtered off, washed with petroleum ether, and dried. The crude product amounted to 1.3 g (45%). After recrystallization from benzene it melted at 193-194°, and admixture of the substance obtained in the preceding experiment caused no depression of melting point. Found: C 41.34; 41.50; H 4.92; 4.80; Fe 18, 96; 19.20; Cl 12.57; 12.56%. $(C_8H_7O_2)_2FeCl$. Calculated: C 41.46; H 4.87; Fe 19.30; Cl 12.25%.

Preparation of Iron Bisbenzoylacetone Chloride

a) From Iron Bisacetylacetone Chloride. A mixture of 1.62 g (0.01 mole) of benzoylacetone in 1 ml of benzene and 1.45 g (0.005 mole) of iron bisacetylacetone chloride in 2 ml of benzene was heated to 50° under a residual pressure of 100 mm; acetylacetone and benzene slowly distilled off. Addition of benzene to the reaction mixture and distillation were repeated until the distillate gave no coloration with ferric chloride (45 hours). Solvent was distilled off at 40-45° under reduced pressure. Crystallization from benzene gave 1.05 g (50%) of product, m.p. 199-200° (decomp.). Found: C 58.19; 58.12; H 4.44; 4.41; Fe 13.87; 13.81; Cl 8.41; 8.74%.

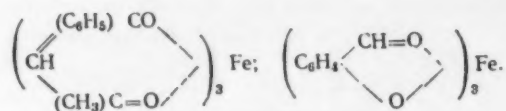
Iron bisbenzoylacetone chloride is a dark-red crystalline substance, readily soluble in benzene and alcohol, but insoluble in petroleum ether and diethyl ether.

b) Reaction of Iron Trisbenzoylacetone with Ferric Chloride. A mixture of 2.15 g (0.004 mole) of iron trisbenzoylacetone and 0.32 g (0.002 mole) of anhydrous ferric chloride in benzene solution was stirred for 3.5 hours at 45-50°. After the usual treatment we obtained 1 g of substance (40% yield). After two crystallizations the substance had m.p. 198-199° (decomp.). Found: C 58.15; 58.00; H 4.52; 4.35; Fe 13.75; 13.39; Cl 8.23; 8.21%. $(C_{10}H_9O_2)_2FeCl$. Calculated: C 58.05; H 4.38; Fe 13.51; Cl 8.57%.

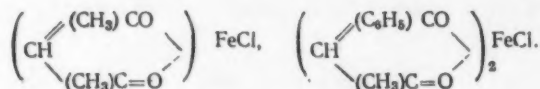
c) Action of Acetyl Chloride on Iron Trisbenzoylacetone. A benzene solution of 2.69 g (0.005 mole) of iron trisbenzoylacetone was heated with 0.39 g (0.005 mole) of acetyl chloride for three hours. The reaction mixture was filtered; after a time crystals were precipitated from the clear filtrate. After being washed with benzene and petroleum ether the crystalline product amounted to 0.65 g (31%) and had m.p. 199-200° (decomp.). The melting point of the substance was not affected by crystallization from benzene. Mixtures of this sample with the products of the preceding two experiments melted without depression.

SUMMARY

1. Iron trisacetylacetone undergoes double decomposition with benzoylacetone and with salicylaldehyde with formation of the corresponding chelate iron compounds:



2. Reverse-disproportionation reactions occur between ferric chloride and iron trisacetylacetone and benzoylacetone, taken in the molar ratio 1:2, with the formation of the corresponding iron monochlorides:



3. Reaction of iron trisacetylacetone and of iron trisbenzoylacetone with acetyl chloride results in the replacement of one chelate residue by chlorine.

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NEW METHOD FOR THE PREPARATION OF ALKOXY ZIRCONIUM COMPOUNDS

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and A. N. Nesmeyanov

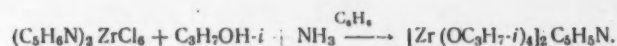
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Translated from *Izvestiya Akademii Nauk SSSR, Otdelenie*

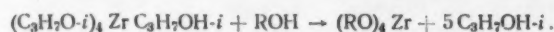
Khimicheskikh Nauk, No. 1, pp. 63-67, January, 1960

Original article submitted June 17, 1958

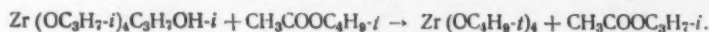
Tetraalkyl orthozirconates and alkoxychlorozirconiums have received very little study. For the synthesis of tetraalkyl orthozirconates British chemists [1] used the reaction of zirconium tetrachloride with alcohols in presence of ammonia. These authors noted some disadvantages of this method, e.g. low yield, difficulty in the isolation of a pure product, and inapplicability of the method to the preparation of sec- and tert-alkyl orthozirconates. This method was substantially modified [2] by replacing the difficultly purifiable zirconium tetrachloride by pyridine hexachlorozirconate, which is readily accessible in the pure state. The latter is prepared from zirconium tetrachloride and pyridine. In the case of isopropyl alcohol the process proceeds via the formation of double salts:



After two crystallization of isopropyl alcohol a double compound of composition $Zr(OC_3H_7 \cdot i)_4 C_3H_7OH \cdot i$ is formed; by heating this at 100° we may isolate pure $Zr(OC_3H_7 \cdot i)_4$. Double decomposition of tetraisopropyl orthozirconates with alcohols leads to other tetraalkyl orthozirconates:

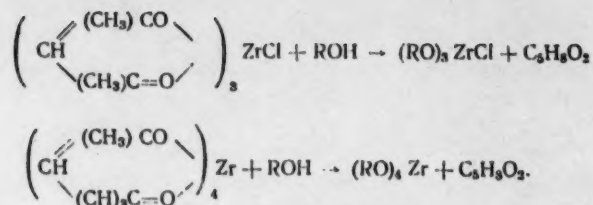


In 1954 Mehrotra [3] showed that by reaction of esters with tetraethyl and tetraisopropyl orthozirconates, tetraalkyl orthozirconates containing sec- and tert-alkyl groups can be prepared, e.g.,



By these methods tetraalkyl orthozirconates $Zr(OR)_4$ (R = alkyl groups from ethyl to n-octyl) were prepared; also some isoalkyl zirconates. The authors succeeded in crystallizing the lower tetraalkyl zirconates by crystallization or vacuum distillation, but already with the hexyl ester distillation could not be carried out without decomposition at 300° and 0.5 mm. The trialkoxychlorozirconiums described in the literature [4] $[(RO)_3ZrCl]$; R = CH₃, C₂H₅, C₃H₇-i, C₅H₁₁-i] were prepared from tetraalkyl orthozirconates synthesized by the above-described methods.

In the present paper we describe a new method for the synthesis of trialkoxychlorozirconiums and tetraalkyl orthozirconates; it consists of the double decomposition of zirconium trisacetylacetonate chloride and of zirconium tetrakisacetylacetonate, respectively, with alcohols:



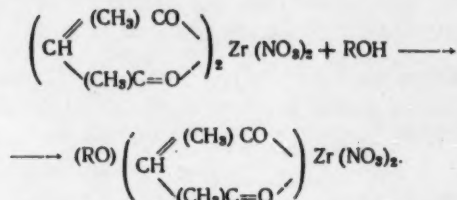
In which R = alkyl.

We have previously described [5] an exchange reaction between zirconium tetrakisacetylacetonate and butyl and benzyl alcohols with formation of the corresponding ortho esters. It was found that this reaction is general and can be used for preparative purposes. By this method we prepared tetrahexyl, tetraheptyl, tetraoctyl, and tetranonyl orthozirconates. Advantages of this method are the accessibility of zirconium tetrakisacetylacetonate, its relative stability toward atmospheric moisture, and the ease of its preparation in the pure state. In the case of the higher alcohols, reaction is complete in two or three hours. We succeeded in distilling all the tetraalkyl zirconates at 10^{-6} mm. In a similar way, by the action of alcohols on zirconium trisacetylacetonate chloride we obtained chlorotripropoxy-, tributoxychloro-, chlorotrihexyloxy-, chlorotrisheptyloxy-, chlorotrisoctyloxy-, and chlorotrisnonyloxy-zirconiums. For the higher alcohols this reaction is also complete in two or three hours.

The resulting trialkoxychlorozirconiums were distilled in a high vacuum. It should be noted that with long heating in a high vacuum the high-boiling compounds synthesized undergo partial decomposition, so that these substances should be distilled in small portions. The compounds synthesized are viscous liquids, readily soluble in the cold in alcohol, benzene, petroleum ether, diethyl ether, chloroform, and other organic solvents; they are sensitive to atmospheric moisture.

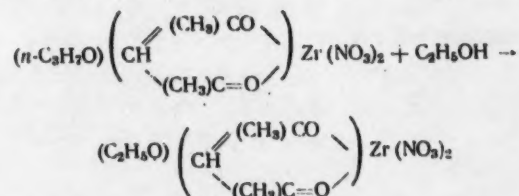
The application of this reaction to zirconium bisacetylacetonate dichloride did not appear to be desirable because of the poor accessibility of this compound. As we have shown previously, dinitrates of chelate zirconium compounds are much more accessible [6]. Zirconium bisacetylacetonate dinitrate was prepared from acetylacetone and zirconium nitrate.

When zirconium bisacetylacetonate dinitrate reacted with propyl and butyl alcohols under transesterification conditions, only one chelated residue was replaced by alkoxyl. The reaction may be represented by the scheme:



in which R = $n\text{-C}_3\text{H}_7$; $n\text{-C}_4\text{H}_9$. We thus succeeded in preparing previously unknown zirconium compounds containing alkoxyl and chelating groups simultaneously.

The alkoxyzirconium acetylacetonate dinitrates were used for the preparation of other compounds of this type by reaction with other alcohols. Thus, by the action of ethanol on propoxyzirconium acetylacetonate dinitrate we obtained the corresponding ethoxyl derivative:



These compounds are fusible crystalline substances, soluble in the usual organic solvents.

EXPERIMENTAL

The experiments were carried out with dry substances under conditions excluding access of atmospheric moisture.

Reaction of Zirconium Tetrakisacetylacetonate with Alcohols

Tetrahexyl Orthozirconate. Excess of hexyl alcohol was added to 3.25 g of zirconium tetrakisacetylacetonate. The reaction mixture was heated at 140-145° under reduced pressure so that acetylacetone and excess of hexyl alcohol distilled off; the reaction lasted six hours (negative test with aqueous ferric chloride solution). After removal of traces of hexyl alcohol at 1 mm and 130° we obtained 2.9 g of viscous product. The substance was distilled at 10^{-5} mm. Found: C 57.90; 57.95; H 10.39; 10.19; Zr 18.07; 18.31%. $(C_6H_{13}O)_4Zr$. Calculated: C 58.11; H 10.58; Zr 18.40%.

Tetraheptyl Orthozirconate. Reaction between 3 g of zirconium tetrakisacetylacetonate and excess of heptyl alcohol was carried out at about 140° under reduced pressure and lasted for three hours. The viscous product (3.1 g) was distilled at about 10^{-5} mm. Found: C 60.88; 60.68; H 11.16; 10.94; Zr 16.40; 16.42%. $(C_7H_{15}O)_4Zr$. Calculated: C 60.89; H 10.96; Zn 16.53%.

Tetraoctyl Orthozirconate. The procedure was similar. Reaction was complete in two hours at 145-155° under reduced pressure. From 3 g of zirconium tetrakisacetylacetonate we obtained 3.3 g of viscous product, which was distilled at about 10^{-5} mm. Found: C 63.65; 63.30; H 11.34; 11.11%. $(C_8H_{17}O)_4Zr$. Calculated: C 63.19; H 11.38%.

Tetranonyl Orthozirconate. The procedure was similar. The exchange reaction between 3.5 g of zirconium tetrakisacetylacetonate and excess of nonyl alcohol lasted for 2.5 hours. The resulting fairly mobile liquid was distilled at about 10^{-5} mm. Found: C 64.88; 65.05; H 11.25; 11.11; Zr 13.45; 13.90%. $(C_9H_{19}O)_4Zr$. Calculated: C 65.08; H 11.54; Zr 13.74%.

Reaction of Zirconium Trisacetylacetonate Chloride with Alcohols

Chlorotripropoxyzirconium. A mixture of 5 g of zirconium trisacetylacetonate chloride and 30 ml of propanol was heated slowly to distill off acetylacetone and excess of propyl alcohol. After eight hours a test for the presence of acetylacetone in the reaction mixture (with aqueous ferric chloride solution) gave a negative result. The product was freed from traces of solvent at 70° under reduced pressure. The viscous liquid product amounted to 3.5 g (quantitative yield). It was distilled at 10^{-4} mm. Found: C 35.81; 35.17; H 6.99; 6.67; Zr 29.65; 29.77; Cl 11.89; 11.70%. $(C_3H_7O)_3ZrCl$. Calculated: C 35.54; H 6.98; Zr 30.02; Cl 11.67%.

Tributoxychlorozirconium. The procedure was similar. From 4 g of zirconium trisacetylacetonate chloride and 30 ml of butyl alcohol we obtained 2.5 g (75%) of a viscous product. It was distilled at 10^{-3} mm. Found: C 41.62; 41.84; H 7.41; 7.95; Zr 26.40; 26.55; Cl 10.75; 10.31%. $(C_4H_9O)_3ZrCl$. Calculated: C 41.63; H 7.86; Zr 26.37; Cl 10.25%.

Chlorotrishexyloxyzirconium. Hexyl alcohol (40 ml) was added to 3.5 g of zirconium trisacetylacetonate chloride. The reaction was carried out at 118-120° and 135-140 mm and was complete in 5.5 hours. The resulting viscous mass (3.4 g) was distilled at about 10^{-5} mm. Found: C 50.07; 50.24; H 8.97; 8.93; Zr 21.36; 21.17%. $(C_6H_{13}O)_3ZrCl$. Calculated: C 50.23; H 9.14; Zr 21.21%.

Chlorotrisheptyloxyzirconium. From 3.6 g of zirconium trisacetylacetonate chloride and heptyl alcohol at 135-140° and 180-185 mm we obtained 3.7 g of viscous product. The reaction lasted for 2.5 hours. The product was distilled at about 10^{-5} mm. Found: C 53.25; 53.40; H 9.46; 9.65; Zr 19.75; 19.64; Cl 7.26; 7.30%. $(C_7H_{15}O)_3ZrCl$. Calculated: C 53.39; H 9.61; Zr 19.33; Cl 7.51%.

Chlorotrisoctyloxyzirconium. From 3 g of zirconium trisacetylacetonate chloride and 20 ml of octyl alcohol we obtained 3 g of viscous product. The reaction lasted for 90 minutes. The product was distilled at about 10^{-5} mm. Found: C 55.70; 55.84; H 10.08; 10.12; Zr 18.54; 18.43%. $(C_8H_{17}O)_3ZrCl$. Calculated: C 56.02; H 9.96; Zr 17.75%.

Chlorotrisnonyloxyzirconium. From 3 g of zirconium trisacetylacetonate chloride and 25 ml of nonyl alcohol we obtained 3.5 g of a fairly mobile oil. The reaction lasted for 90 minutes. Found: C 58.41; 58.55; H 10.22; 10.10; Zr 16.25; 16.66; Cl 6.36; 6.13%. $(C_9H_{19}O)_3ZrCl$. Calculated: C 58.25; H 10.34; Zr 16.40; Cl 6.37%.

Reaction of Zirconium Bisacetylacetonate Dinitrate with Alcohols

Propoxyzirconium Acetylacetonate Dintrate. A solution of 19.4 g of zirconium bisacetylacetonate dintrate in 80 ml of propyl alcohol was heated slowly to 85-90° at 180-185 mm, and a mixture of acetylacetone and propyl alcohol distilled off. After eight hours acetylacetone could no longer be detected in the distillate, but a test for acetylacetone in the reaction mixture was positive. Further addition of propyl alcohol and heating did not result in complete removal of acetylacetone. The residue was freed from traces of propyl alcohol, carefully washed with cold benzene and petroleum ether, and dried in a stream of dry air. The crude product amounted to 10 g (57%). The product was crystallized twice from benzene and freed from traces of solvent by heating it for two hours at a residual pressure of 1 mm in an Abderhalden pistol. The substance melted at 149-150° (melting preceded by sintering)*. Found: C 25.94; 26.10; H 3.74; 3.81; Zr 24.66; 24.86; N 7.75%; 7.74% ($C_8H_7O_2)(C_3H_7O)Zr \cdot (NO_3)_2$. Calculated: C 25.72; H 3.78; Zr 24.44; N 7.50%.

Propoxyzirconium acetylacetonate dinitrate is soluble in benzene and chloroform, but insoluble in petroleum ether and diethyl ether. It hydrolyzes in moist air.

Butoxyzirconium Acetylacetonate Dinitrate. From 6.5 g of zirconium bisacetylacetonate dinitrate and 65 ml of butyl alcohol at 90-95° and 180 mm we obtained (after removal of solvent by distillation) 7.3 g of crude product in the form of a greasy mass containing crystals. Treatment as described for the preceding experiment gave 2.85 g (46%) of product. After crystallization from benzene and drying in an Abderhalden pistol the substance melted at 144-146° (melting preceded by sintering). Found: Zr 23.50; 23.44; N 7.42; 7.62%. (C_8H_9O) ($C_5H_7O_2$) \cdot Zr(NO_3) $_2$. Calculated: Zr 23.56; N 7.23%.

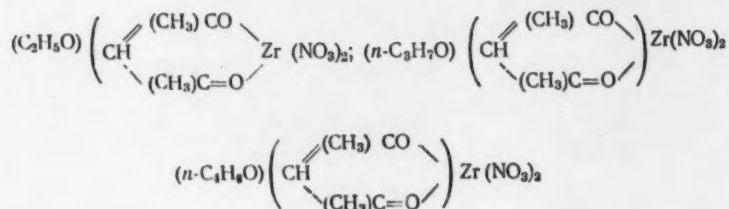
Butoxyzirconium acetylacetonate dinitrate is similar in properties to the above-described propoxy compound.

Reaction of Propoxyzirconium Acetylacetonate Dinitrate with Ethanol

Propoxyzirconium acetylacetonate dinitrate (5 g) was dissolved in 50 ml of ethanol (heating to 85-90°). A mixture of ethyl and propyl alcohols was slowly distilled from the solution under reduced pressure. The reaction lasted for ten hours. After removal of most of the ethanol the solid residue was filtered off, washed with benzene and petroleum ether, and dried; weight 2.1 g (43%). The product was crystallized from benzene and freed from traces of solvent by vacuum treatment in an Abderhalden pistol for three hours. The substance melted, after decomposition, at 148-152°. Found: C 23.42; 23.55; H 3.42; 3.47; Zr 25.68; 25.53; N 8.01; 8.17%. $(C_2H_5O) \cdot (C_5H_7O_2)_2 Zr(NO_3)_2$. Calculated: C 23.38; H 3.36; Zr 25.39; N 7.79%.

SUMMARY

1. The first mixed zirconium compounds containing both chelating groups and alkoxy groups were prepared:



2. By exchange reactions between zirconium trisacetylacetonate chloride and alcohols we obtained chloroalkoxyzirconiums of the type $(RO)_3ZrCl$ ($R = n-C_3H_7$, $n-C_4H_9$, $n-C_6H_{13}$, $n-C_7H_{15}$, $n-C_8H_{17}$, $n-C_9H_{19}$).
3. By exchange reactions between zirconium tetrakisacetylacetonate and hexyl, heptyl, octyl, and nonyl alcohols we obtained the corresponding tetraalkyl orthozirconates $(RO)_4Zr$.

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*Original Russian pagination. See C. B. translation.

DIENE SYNTHESIS

COMMUNICATION 2. STUDY OF DIENE CONDENSATIONS OF p-BENZOQUINONE AND 1,4-NAPHTHOQUINONE BY THE SPECTROPHOTOMETRIC METHOD

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Translated from Akademii Nauk SSSR, Otdelenie

Khimicheskikh Nauk No. 1, pp. 68-72, January, 1960

Original article submitted May 14, 1958

In the preceding investigation [1] we showed that it is possible to use a spectrophotometric method for the detection of intermediate compounds in diene condensations in the case of the reactions of maleic anhydride with various dienes. It was of interest to study reactions with other dienophiles. In the present investigation we studied reactions in which p-benzoquinone and 1,4-naphthoquinone served as dienophiles. It should be noted that for p-benzoquinone, as in the case of maleic anhydride, 1:1 molecular complexes with aromatic compounds such as benzene are known, and these show absorption in the ultraviolet [2]. As dienes we used cyclopentadiene, isoprene, and piperylene (mixture of isomers). The experimental procedure was as before [1].

The spectra were determined with an SF-4 spectrophotometer in a 1-cm cell. All the substances used were purified by distillation or crystallization. The diene-condensation products used in the work were prepared by methods described in the literature: mono adducts of p-benzoquinone with cyclopentadiene [3], isoprene [4], and piperylene [5]; bis adducts of p-benzoquinone with cyclopentadiene [3] and isoprene [6]; and adducts of 1,4-naphthoquinone with cyclopentadiene [3] and isoprene [6].

It is known that the reaction of p-benzoquinone with dienes proceeds in two stages. First one molecule of the diene adds to p-benzoquinone and a monoadduct is formed. The monoadduct then reacts with a second molecule of diene and gives a bisadduct. The bis adduct of cyclopentadiene is readily obtained at low temperatures [3], whereas the bis adduct of isoprene is obtained by heating for 10-12 hours at 100° [6]. A bis adduct of p-benzoquinone with piperylene has not been prepared.

In accordance with the above we investigated solutions of p-benzoquinone in dienes and solutions of mono adducts in the corresponding dienes, for it may be expected that the formation of intermediate compounds will precede both the formation of the mono adduct and that of the bis adduct. In a solution of p-benzoquinone in cyclopentadiene at room temperature (Fig. 1) an intense absorption arises in the region of 290 m μ (molecular compounds of p-benzoquinone with aromatic compounds absorb in approximately the same region [2]). The intensity of this absorption falls with time, and the spectrum approximates to that of the bis adduct of p-benzoquinone with cyclopentadiene. The mono adduct absorbs much more feebly in this region, and the intense absorption can therefore be attributed only to the formation of an intermediate compound. However, from the changes in the spectrum it is impossible to say whether its formation precedes that of the mono adduct or bis adduct. Further data are provided by the spectrum of a solution of the mono adduct of p-benzoquinone with cyclopentadiene in cyclopentadiene (Fig. 2). Here again there at first arises absorption corresponding to the molecular complex, and the intensity of this falls with time so that the spectrum as a whole approximates to that of the bis adduct. It is quite evident that the reaction of the mono adduct with cyclopentadiene passes through the stage of the formation of an intermediate molecular compound. From a comparison of the initial intensities (Figs. 1 and 2), we may suppose that, in the case of p-benzoquinone also, a complex with cyclopentadiene is first formed and then passes into the mono adduct.

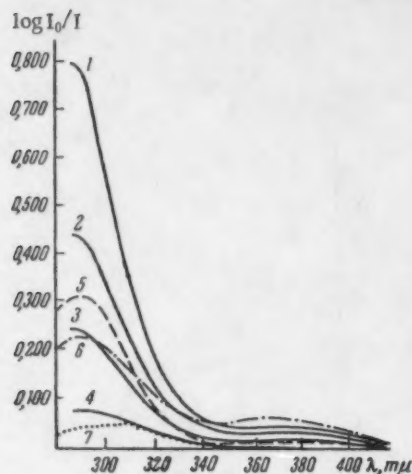


Fig. 1. Ultraviolet absorption spectra of 0.000875 M solution of p-benzoquinone in 9 : 1 (by volume) cyclopentadiene-chloroform: 1) 3 min. after mixing; 2) after 15 min.; 3) after 45 min.; 4) after 180 min.; 5) spectrum of p-benzoquinone; 6) spectrum of mono adduct; 7) spectrum of bis adduct of p-benzoquinone with cyclopentadiene in chloroform.

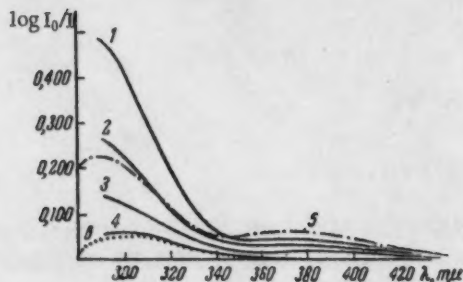


Fig. 2. Ultraviolet absorption spectra of 0.000869 M solution of mono adduct of p-benzoquinone with cyclopentadiene in 9 : 1 (by volume) cyclopentadiene-chloroform: 1) 4 min. after mixing; 2) after 10 min.; 3) after 45 min.; 4) after 90 min.; 5) spectrum of mono adduct; 6) spectrum of bis adduct of p-benzoquinone with cyclopentadiene in chloroform.

mono adduct forms only the intermediate complex with isoprene, and reaction does not go further. Only with heat is the complex converted into the bis adduct. From this the behavior of p-benzoquinone in isoprene becomes clear. The mono adduct is formed through the stage of the intermediate compound, and then a complex of the mono adduct with isoprene is formed which does not change further at room temperature.

From the spectra of solutions of p-benzoquinone in piperylene (Fig. 5) and of the mono adduct of p-benzoquinone with piperylene in piperylene (Fig. 6) it is seen that the reaction of p-benzoquinone with piperylene proceeds analogously. In this case the mono adduct, which is again formed via an intermediate complex, gives a molecular compound with piperylene. No further changes were observed in the spectrum of the solution of p-benzoquinone in piperylene, even after a week.

Hence, the reaction of p-benzoquinone with the dienes studied proceeds in stages: p-benzoquinone + diene intermediate complex of p-benzoquinone with diene → mono adduct → intermediate complex of mono adduct with diene → bis adduct. We must mention that the difference of the spectrum of the mono adduct of p-benzoquinone with piperylene from the spectra of the mono adducts of p-benzoquinone with isoprene and cyclopentadiene was somewhat unexpected.

Fig. 7 gives the spectrum of a solution of 1,4-naphthoquinone in cyclopentadiene. The reaction of 1,4-naphthoquinone with cyclopentadiene proceeds vigorously and, judging from the spectra, after ten minutes all the naphthoquinone in the solution has been converted into the adduct. Formation of an intermediate complex in the solution is indicated by the rise in Curve 1 in the region of 290 mμ. In the spectra of solutions of 1,4-naphthoquinone in isoprene (Fig. 8) and piperylene (Fig. 9) no absorption indicative of the formation of an intermediate compound was found. However, this does not prove that the intermediate compound is not formed during the reaction. It is quite possible that the rate of conversion of the complex into the adduct exceeds the rate of formation of the complex itself, so that absorption attributable to the complex cannot be observed.

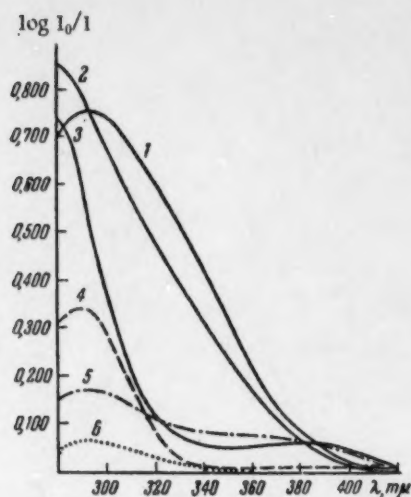


Fig. 3. Ultraviolet absorption spectra of 0.000947 M solution of p-benzoquinone in 9:1 (by volume) isoprene-chloroform: 1) 4 min. after mixing; 2) after 2 hours; 3) after 20 hours; 4) spectrum of p-benzoquinone; 5) spectrum of mono adduct; 6) spectrum of bis adduct of p-benzoquinone with isoprene in chloroform.

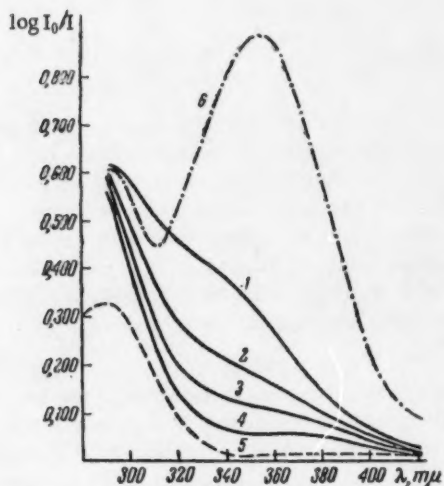


Fig. 5. Ultraviolet absorption spectra of 0.000924 M solution of p-benzoquinone in 9:1 (by volume) piperylene-chloroform: 1) 4 min. after mixing; 2) after 1 hour; 3) after 2 hours; 4) after 15 hours; 5) spectrum of p-benzoquinone; 6) spectrum of mono adduct of p-benzoquinone with piperylene in chloroform.

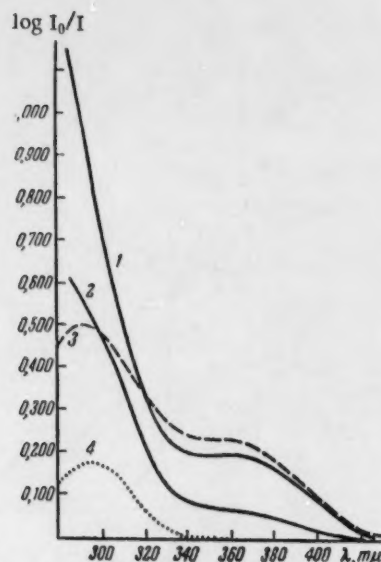


Fig. 4. Ultraviolet absorption spectra of 0.00282 M solution of mono adduct of p-benzoquinone with isoprene in 1:1 (by volume) isoprene-chloroform: 1) 5 min. after mixing and after 24 hours; 2) after heating for 3 hours at 100°; 3) spectrum of mono adduct; 4) spectrum of bis adduct in chloroform.

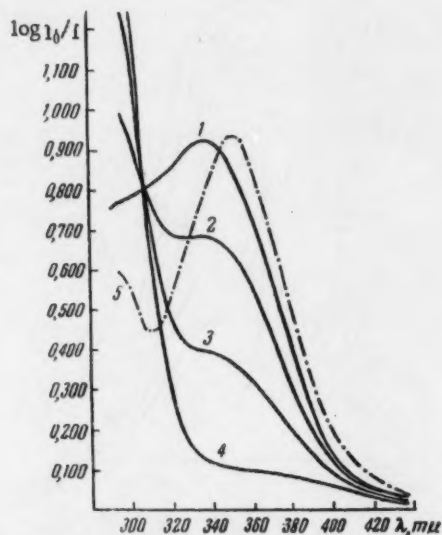


Fig. 6. Ultraviolet absorption spectra of 0.000909 M solution of mono adduct of p-benzoquinone with piperylene in piperylene: 1) 5 min. after mixing; 2) after 2 hours; 3) after 6 hours; 4) after 24 hours; 5) spectrum of mono adduct in chloroform.

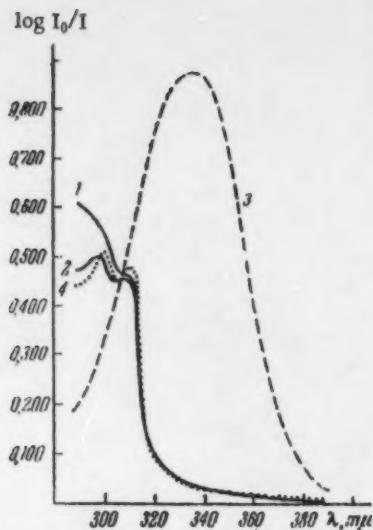


Fig. 7. Ultraviolet absorption spectra of 0.000304 M solution of 1,4-naphthoquinone in 4:1 (by volume) cyclopentadiene-chloroform: 1) 3 min. after mixing; 2) after 10 min. and 14 hours; 3) spectrum of 1,4-naphthoquinone; 4) spectrum of adduct of 1,4-naphthoquinone with cyclopentadiene in chloroform.

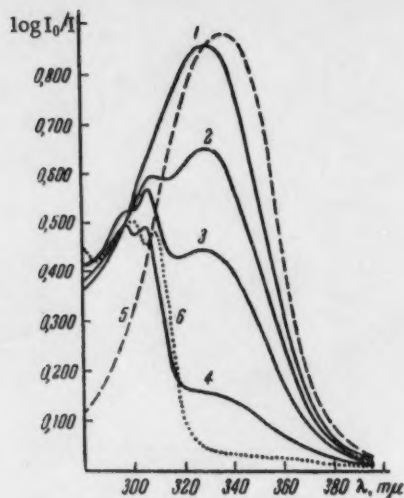


Fig. 8. Ultraviolet absorption spectra of 0.000304 M solution of 1,4-naphthoquinone in 4:1 (by volume) isoprene-chloroform: 1) 5 min. after mixing; 2) after 17 hours; 3) after 42 hours; 4) after 90 hours; 5) spectrum of 1,4-naphthoquinone; 6) spectrum of adduct of 1,4-naphthoquinone with isoprene in chloroform.

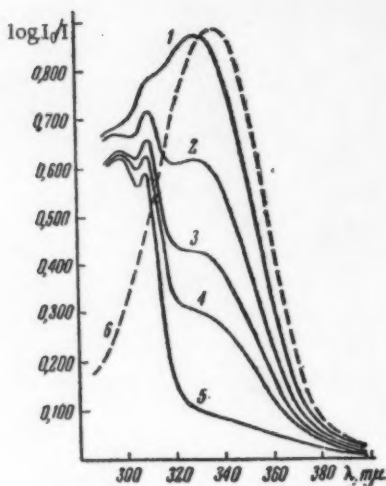


Fig. 9. Ultraviolet spectra of 0.000304 M solution of 1,4-naphthoquinone in 4:1 (by volume) piperylene-chloroform: 1) 5 min. after mixing; 2) after 1 hour; 3) after 2 hours; 4) after 3 hours; 5) after 10 hours; 6) spectrum of 1,4-naphthoquinone in chloroform.

SUMMARY

1. It was shown by the spectrophotometric method that, in the reactions of p-benzoquinone with cyclopentadiene, isoprene, and piperylene, the formation both of the mono adduct and of the bis adduct is preceded by the formation of intermediate compounds. In the case of isoprene and piperylene, reaction at room temperature stops at the stage of the formation of the molecular complex of the monoadduct with the diene.

2. The reaction of 1,4-naphthoquinone with cyclopentadiene passes through the stage of the formation of an intermediate compound. In solutions of 1,4-naphthoquinone in isoprene and piperylene no absorption attributable to a complex was observed, possibly because the rate of conversion of the complex into the adduct exceeds the rate of formation of the complex.

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CATALYTIC SYNTHESIS OF ISOPRENE FROM HYDROCARBON GASES

COMMUNICATION 2. SYNTHESIS OF ISOPRENE FROM PROPENE

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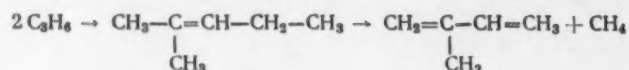
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Translated from *Izvestiya Akademii Nauk SSSR, Otdelenie*

Khimicheskikh Nauk No. 1, pp. 73-79, January, 1960

Original article submitted May 7, 1958

Considerable interest is presented by the two-stage scheme for the preparation of isoprene from propene only, namely, by heterogeneous catalytic dimerization of the propene, mainly to 2-methyl-2-pentene, and subsequent thermal decomposition into isoprene and methane:



This process, which was proposed in 1946 by Gorin and Oblad [1], is valuable with respect both to the utilization of propene and to the production of isoprene, in spite of its two-stage character.

The first stage of the process has been studied in greater detail than the second. According to the patent [1], the catalytic dimerization of propene proceeds at 1-3 atm and 360° over an aluminum silicate catalyst. The yield of dimer attains 45.8% on the propene that reacts and 42.8% on the propene that is passed. The product consists of 7% of C_5 hydrocarbons, 36.7% of propene dimer (a mixture of 2-methyl-2-pentene, 2-methyl-1-pentene, and 3-methyl-2-pentene), 15.7% of C_7 hydrocarbons, 8.6% of C_8 hydrocarbons, 11.4% of C_9 hydrocarbons, and 17.4% of C_{10} and higher hydrocarbons.

The catalytic polymerization of propene was studied by Gayer [2], who showed that the reactions proceed at atmospheric pressure at 300-360° over a catalyst of about 1% of alumina on silica gel. The yield of propene dimer was greatly dependent on the space velocity and attained a maximum of 31% at a feed of 1.4 g of propene per gram of catalyst per hour. However, the catalyst did not have satisfactory stability and its activity fell from 0.6 to 0.2 g of polymer per gram of catalyst in the course of 160-170 hours. A similar catalyst was used by Kazanskii and Rozengart [3] for the polymerization of isobutene. It has been found recently that addition of oxides of cobalt, molybdenum, nickel, and other metals to a catalyst of the Gayer type raises its stability and favors increase in the amount of light fraction in the product [4-7].

The second stage of the process, the pyrolysis of 2-methyl-2-pentene to isoprene, was examined in the patent [1]. There are no other references in the literature to the obtaining of isoprene in this way, though considerable attention has been given to the pyrolysis of pentenes and butenes [8]. In the thermal decomposition, the propene dimer fraction of b.p. 60-70°, which contains 80% of 2-methyl-2-pentene (36.7% of the whole of the polymer), was diluted with 10% of nitrogen or steam and passed through a reactor at 775-825° with a contact time

TABLE 1

Catalytic Polymerization of Propene

Expt.	Catalyst	Composition of catalyst	Wt. catalyst (g)	Temp. of expt. (°C)	Space velocity (g C ₃ H ₆ per g catalyst per hr)	Wt. polymer per g catalyst per hr	Yield polymer (%)
1	1	MgO + Al ₂ O ₃ /SiO ₂	26	330	0,36	0,028	8,0
2					0,27	0,019	8,9
3					0,53	0,018	3,4
4					0,16	0,031	18,9
5	2	ZnO + Al ₂ O ₃ /SiO ₂	11	330	0,51	0,218	41,9
6					0,88	0,013	5,2
7					0,24	0,058	24,0
8	3	Cr ₂ O ₃ + Al ₂ O ₃ /SiO ₂	17	345	1,90	0,176	8,3
9					0,52	0,226	42,1
10					0,50	0,086	17,5
11					0,39	0,076	19,3
12	4	Fe ₂ O ₃ + Al ₂ O ₃ /SiO ₂	15	325	1,10	0,203	17,2
13					0,24	0,080	30,3
14					0,41	0,080	19,5
15	5	ASC	33	340	0,43	0,067	15,6
16					0,30	0,095	31,8
17					0,76	0,047	6,2
18	6*	Al ₂ O ₃ / ASC	33	340	0,40	0,082	20,6
19					0,41	0,083	19,9
20			23	340	0,34	0,01	32,4
21					0,98	0,290	30,6
22					0,71	0,229	32,2
23					0,77	0,212	27,3
24	7**	Al ₂ O ₃ / ASC	39	340	0,26	0,087	33,6
25					0,32	0,084	26,9
26					0,25	0,065	25,5
27	8***	Al ₂ O ₃ / ASC	25	340	0,92	0,140	15,6
28					0,97	0,120	12,5
29					1,09	0,110	10,3
30					1,41	0,064	4,5
31	9	TiO ₂ / ASC	14	420	2,67	0,470	17,8
32					2,17	0,730	14,1
33					3,37	0,640	11,6
34					4,37	0,70	11,8
35	10	Ce ₂ O ₃ + TiO ₂ / ASC	21	440	0,57	0,260	27,1
36					1,66	0,300	18,2
37					0,56	0,140	25,1

*Double impregnation with 0.16 N aluminum sulfate.

** Single impregnation with 0.16 N aluminum sulfate.

*** Double impregnation with 6.6 N aluminum sulfate.

of 0.005-2 seconds and a total pressure which was 0.1 atm less than the partial pressure of the original dimer. The yield of isoprene on the amount of dimer decomposed was 46.7 %; the C₅ fraction contained 95% of isoprene. Hence, the yield of isoprene in the two-stage process, calculated on the original propene that reacted, was 21.4%.

In the present investigation we studied the possibility of preparing isoprene from propene only via propene dimer. The conditions used differed from those described in the patent in that the reaction was carried out at atmospheric pressure, a fact which presents some interest on its own account.

EXPERIMENTAL

Experiments on the dimerization of propene were carried out at atmospheric pressure in the apparatus described in the preceding communication. The pyrolysis of propene dimer was carried out in a flow system under reduced pressure. The reactor consisted of a quartz tube of diameter 3 mm with a working volume of 0.92 cc. Heating was carried out in a three-bar silit furnace. The dimer vapor was fed to the reactor in a stream of

dry nitrogen or pure carbon dioxide from a thermostatically controlled cylindrical evaporator. The amount and the rate of passage of the gas was measured with the aid of a gas meter and flow meter. A constant pressure was maintained in the system by means of a manostat.

Many different compounds were examined as catalysts; of these, only ten were found to be active in the dimerization of propene; they are enumerated below with the methods of preparation.

Catalyst 1: $\text{MgO} + \text{Al}_2\text{O}_3 / \text{SiO}_2$. This was prepared by Gayer's method [2] with further treatment of the catalyst with magnesium nitrate. To 100 ml of water-glass (sp.gr. 1.40) diluted with 100 ml of water we added a 20% excess of 5 N HCl. The precipitate was washed free from Cl^- ions and treated with 200 ml of 0.2 N aluminum sulfate with heating in a water bath for 1-2 hours. The precipitate was washed free from sulfate ions by repeated washing with distilled water; it was dried and treated with 100 ml of 5% magnesium nitrate solution and then with 100 ml of 3% ammonia solution. After removal of nitrate ions, the catalyst was dried at 100° and roasted at the temperature of the experiment. **Catalyst 2:** $\text{ZnO} + \text{Al}_2\text{O}_3 / \text{SiO}_2$. This was prepared analogously, but impregnation was with 5% zinc nitrate solution. **Catalyst 3:** $\text{Cr}_2\text{O}_3 + \text{Al}_2\text{O}_3 / \text{SiO}_2$. This was prepared analogously, but impregnation was with 5% chromium nitrate solution. **Catalyst 4:** $\text{Fe}_2\text{O}_3 + \text{Al}_2\text{O}_3 / \text{SiO}_2$. This was prepared analogously, but impregnation was with 5% ferric nitrate solution. **Catalyst 5:** aluminum silicate catalyst (ASC) (see Communication 1). This was activated in a stream of air at 450° . **Catalyst 6:** $\text{Al}_2\text{O}_3 / \text{ASC}$. Catalyst ASC was treated for two hours with 0.16 N aluminum sulfate with heating in a water bath. The catalyst was washed free from sulfate ions, dried at 100° , and roasted at the temperature of the experiment. **Catalyst 7:** $\text{Al}_2\text{O}_3 / \text{ASC}$. This was prepared analogously, but with two impregnations with 0.16 N aluminum sulfate. **Catalyst 8:** $\text{Al}_2\text{O}_3 / \text{ASC}$. This was prepared analogously, but with two impregnations with 6.6 N aluminum sulfate. **Catalyst 9:** $\text{TiO}_2 / \text{ASC}$. This was prepared like Catalyst 6, but with replacement of the activating aluminum sulfate solution by 0.2 N titanium sulfate. **Catalyst 10:** $\text{Ce}_2\text{O}_3 + \text{TiO}_2 / \text{ASC}$. This was prepared like the preceding catalyst, but was given additionally a treatment in 0.1 N cerium nitrate.

TABLE 2
Compositions of Catalyzates from Fractionation Data

Hydrocarbon fraction	B.p. of fraction ($^\circ\text{C}$)	Catalyst 6			Catalyst 9; tech. C_3H_6	Constants of fractions (catalyst 6; tech. C_3H_6)		Gayer's data [2] (%)
		tech. C_3H_6	pure C_3H_6 without recirculation	pure C_3H_6 with recirculation		n_D^{20}	d_4^{20}	
1	2	3	4	5	6	7	8	9
C_5	26-50	7,6	10,3	17,4	21,3	1,3835	0,6567	7,1
C_6	50-80	40,3	50,8	42,6	56,7	1,3955	0,6857	39,3
C_7	80-100	16,6	11,6	18,3	8,7	1,4065	0,7098	15,7
C_8 - C_7	26-100	64,5	72,7	72,7	86,7			62,1
2-Methyl-2-pentene	64,5-70		50,0 25,4	53,6 22,8	68,2* 38,7**			
C_8	100-125	7,4	6,9	5,3	3,9	1,4177	0,7340	8,6
C_9	125-150	9,9				1,4262	0,7485	11,4
C_{10}	150-175	17,8	19,3	16,2	9,1	1,4555	0,8064	17,7
Residue	>175							

*(% on C_6 fraction).

**(% on whole polymer).

Two-Stage Synthesis of Isoprene from Propene

a) **Catalytic Dimerization of Propene.** Work on the first stage of the process was directed mainly on the search for an active and stable catalyst for the dimerization of technical propene, capable of preferentially catalyzing the formation of 2-methyl-2-pentene at atmospheric pressure. In view of the fact that this process has already received some investigation, in the present work our main attention was directed to the improvement of existing catalysts for the dimerization of propene, in particular Gayer's catalyst, which we found to be active,

TABLE 3

Pyrolytic Demethanization of Propene Dimer to Isoprene

Rate of feed of dimer (g/min)	Carrier gas (ml(STP)/min)		Ratio of dimer: gas = 1 : v _x	Duration of expt. (mln)	Pressure (mm)	Time of contact (sec)	Conver- sion (%)	Wt. of conden- sate (g)	Composition: % of fraction of b.p.					Yield of isoprene		
	N ₂	CO ₂							22-30°	32-36° (% of isoprene)	36-50°	50-70°	>70°	% on dimer reacted	% on dimer passed	mole per 100 moles of original dimer
0,18	—	—	—	52	760	0,2	71,6	7,8	—	—	—	6,3	4,5	5,56		
0,206	42	—	0,76	90	760	0,015	75,5	5,66	22	5,5	7,8	50,5	13	3,46		
0,14	—	—	—	54	85	0,043	42	8,3	12	9,3	4,3	60	1,7	11,1		
0,109	28	—	1,39	276	460	0,065	81	1,74	6	22,5	15	51	2,7	9,9		
0,13	33,7	—	0,973	117	165	0,048	36	6,66	7	7,8	0,7	82,8	1,5	9,4		
0,19	—	16,7	0,33	58	306	0,09	82,7	4,3	—	5,2	3,5	45,2	5,5	21,2		
0,04	—	18,2	1,67	157	284	0,18	60,9	1,2	6,4	9,6	—	80	9,6	5,8		

but unstable and unsuitable for work in a flow system. In spite of claims in patents [9, 10], the introduction of various substances into this catalyst (1-10% of Be, Ni, Ce, and other oxides), both by coprecipitation and by the impregnation of alkaline silica gel with solutions of the corresponding salts, gave an inactive catalyst of low stability (yield of polymer 3-5% at 300-500°).

The investigation of natural aluminum silicates [11-13] (Rashkov clay, bentonite) revealed that they were of low activity (yield of polymer 3.6-9%).

Catalysts obtained by the hydrolysis of SnCl_4 with subsequent treatment of the gel with a solution of an aluminum or titanium salt were also of low activity (yield 3-8%, 400°) despite the complete absence in this case of sodium zeolite, which is known [11-13] to lower the activity of aluminum silicate catalysts.

Catalysts prepared by the method given in [2], but treated with magnesium, zinc, chromium, or iron salts (Catalysts 1-4, Table 1), were close in activity to the Gayer catalyst. However, as Table 1 shows, though the yield of polymer was higher than in Gayer's experiments (30-40% and 20-30%, respectively), these catalysts had inadequate productivity, i.e., at a space velocity of 1-1.6 g of propene per gram of catalyst per hour the yield of polymer was below that given in the literature. Table 1 shows that these catalysts were of low stability, but were nevertheless more stable than Gayer's catalyst. Also, these catalysts were readily regenerated by removal of the carbonaceous film from the catalyst surface by passage of dry air at a temperature 70° above that of the experiment. This method was found to be much more convenient than that proposed by Gayer, which amounted, in fact, to the preparation of a new catalyst [2].

Catalysts based on the aluminum silicate catalyst ASC were found to have higher stability. Table 1 shows that Catalyst 5 had relatively high activity and stability and substantially regained its activity after regeneration. Activation of this catalyst with 0.16 N aluminum sulfate by the method given in [2] did not raise the activity of this catalyst greatly and, moreover, lowered its stability. However, a double treatment of Catalyst ASC with 0.16 N aluminum sulfate (Catalyst 6) made it very stable. Many prolonged experiments were carried out over this catalyst in order to determine its stability; its activity did not fall appreciably in 30 hours of continuous work. A double treatment of Catalyst ASC with a more concentrated aluminum sulfate solution (6.6 N) gave Catalyst 8, which also had high stability and productivity, but the yield of product was lower than with Catalysts 6 and 7, which were obtained by treatment with more dilute aluminum sulfate solutions. Following directions in patents [14], we introduced Zr, Ce, and Ti oxides into Catalyst ASC. Only treatment with titanium sulfate gave an active catalyst (Table 1, Catalyst 9). Catalysts containing Zr and Ce oxides showed no advantage over pure ASC. After-treatment of Catalyst 9 with cerium nitrate also gave an active and, what is more important, stable catalyst (Catalyst 10); it was found to be possible to carry out the reaction over this at 440° and the catalyst could be regenerated with ease. It is important to note that these last catalysts (9 and 10) had the advantage not only of easy regeneration, stability, and high activity, but also of promoting the polymerization of propene with formation of the light fraction in greater amount than other catalysts known at present.

In order to compare our results, which were obtained with technical propene, with those reported in the literature, the polymerization of pure propene was investigated over catalyst 6. The reaction was carried out at 340° at a space velocity of 0.4-1.0 g of propene per gram of catalyst per hour (Experiments 21-23, Table 1). To determine the effect of impurities in the original gas on the polymerization, in a series of experiments, unchanged propene was recirculated together with gaseous products. Table 2 gives the compositions of the catalyzates, determined from fractionation data, from the most characteristic experiments with Catalysts 6 and 9. For comparison, the composition of Gayer's catalyzate [2] is given in Table 2. It may be seen that in our experiments more of the light C_6 fraction was obtained (50.8%) and this had a higher content of 2-methyl-2-pentene than was obtained previously (39.3%) [2]. It is interesting that the process can be directed toward the formation of light fractions by the use of Catalyst 9. Even when technical propene is used the content of C_6 fraction is 56.7%, which is higher than the content of this fraction in the catalyzate from pure propene in presence of Catalyst 6. When the latter catalyst was used, the catalyzate fraction of b.p. 50-80° contained 43.8% of 2-methyl-2-pentene (b.p. 63-65°) (23.8% of the whole polymer). The wider dimer fraction of b.p. 62-70° formed 68.2% of the C_6 fraction (38.7% of the whole polymer).

It was thus found that an aluminum silicate catalyst containing small amounts of magnesium, copper, or iron oxide and treated with solutions of aluminum or titanium sulfate promotes the polymerization of technical propene with formation of a catalyzate containing 38% of a fraction of b.p. 62-70° rich in 2-methyl-2-pentene

(68.2%), which can be used as raw material in the second stage of the process: the demethanization of the dimer with formation of isoprene.

b) Pyrolytic Demethanization of Propene Dimer to Isoprene. In order to determine the optimum conditions [1] for the pyrolysis of propene dimer it is necessary to vary the pressure (100-700 mm), temperature (700-900°), time of contact (0.005-2 seconds), proportions of dimer and carrier gas (from 1:10 to 10:1), and the 2-methyl-2-pentene content of the dimer (50-95%). In the present investigation our task was the verification of patent data on the pyrolytic demethanization of the dimer to isoprene and the establishment of the possibility of preparing isoprene by the two-stage scheme. The reaction was carried out at 750° with a slight variation of rate of feed of dimer and a considerable variation in pressure (85-760 mm) and in time of contact (0.015-0.2 second). The time of contact τ was calculated from the formula:

$$\tau = \frac{P_t \cdot T_0}{P_0 (T_0 + t)} - \frac{V_{\text{reactor}}}{\left[\frac{a_{\text{dim}} \cdot 22414}{84} + \frac{273 \cdot V_{N_2}}{273 + t} \right]},$$

in which a_{dim} is the rate of feed of dimer into the reactor (g/second), and V_{N_2} is the rate of feed of carrier gas [ml(STP)/second].

Table 3 gives the results of the most characteristic experiments. In the pyrolysis we used a fraction of b.p. 50-70°, containing 75% of unsaturated hydrocarbons, and having n_D^{20} 1.3955 and d_4^{20} 0.6857. The gas liberated in the pyrolysis consisted of methane (30-40%), ethylene (10-15%), propene (5-8%), and butenes (0.4%); no hydrogen was detected. The condensate obtained in a trap at -78° was slowly brought to 20° and fractionated through a column. The following fractions were collected: 22-30° (mainly cyclopentadiene); 32-36° (isoprene); 36-50° (mainly piperylene); and a fraction of b.p. 50-70° (unchanged dimer). Maleic anhydride adducts were prepared from fractions containing dienes. From the amount of adduct of m.p. 63.0° obtained from the 32-36° fraction the isoprene content of the latter was estimated at 80-85%. In admixture with the adduct (m.p. 63.3-63.7°) prepared from pure isoprene [b.p. 33.0-33.5° (756 mm); d_4^{20} 0.6788] there was no depression of melting point. From the fraction of b.p. 22-30° we isolated a narrower fraction of b.p. 26-30°, from which we prepared a maleic anhydride adduct of m.p. 119°, instead of 165°, as expected for the adduct with cyclopentadiene, which indicates that this fraction is more complex in composition [15]. Hence, it was shown that the pyrolysis of a propene dimer fraction considerably enriched in 2-methyl-2-pentene gives isoprene in a yield that can be raised by the choice of optimum conditions. Under the conditions investigated the maximum yield of isoprene was obtained at 750°, 306 mm, τ = 0.09 second, and a dimer : nitrogen ratio of 1:0.33; it was then 17.7%, or 5.7% on the original propene (the average yield in the dimerization stage being taken as 30%).

SUMMARY

A study was made of the catalytic polymerization of propene, which led to the formation of dimer in 38.7% yield; the dimer could then be subjected to pyrolysis with formation of isoprene in 17.7% yield, calculated on the dimer.

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FREE-RADICAL ADDITION REACTIONS
WITH 1-, 2-, AND 3-ALKENYLSILANES

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Translated from *Izvestiya Akademii Nauk SSSR,*
Otdelenie Khimicheskikh Nauk, No. 1, pp. 80-83,
January 1960

Original article submitted May 14, 1958

Over several years Petrov and co-workers have synthesized various organosilicon compounds containing a double bond in the α , β , γ , and other positions with respect to silicon [1-11]. Qualitative and quantitative differences were noted in the reactivities of these alkenylsilanes in ionic addition reactions. In all cases organosilicon compounds in which the double bond was in the β position were exceptionally active in these reactions. The intensities of the characteristic double bond frequencies of alkenylsilanes in the Raman spectra were found to be least for an α double bond, greatest for a β double bond, and intermediate in value for a γ double bond. Comparison of the calculated and found molecular refractions for the compounds $R_3Si(CH_2)_nCH=CH_2$ showed that there was exaltation for allylsilanes, but none for compounds in which $n = 0, 2, 3, 4$ [11]. Such physical peculiarities of allylsilanes as enhanced intensity of the double bond lines in the Raman and infrared spectra, exaltation of molecular refraction, and higher reactivity in the above-mentioned reactions are probably to be explained by the presence of conjugation between the double bond and the Si-C bond in these compounds [11].

We undertook the present investigation of free-radical addition reactions with 1-, 2-, and 3-alkenylsilanes under comparable conditions to determine the possibilities of this reaction in synthesis and to confirm the occurrence of conjugation of the double bond of allylsilanes with the Si-C bond. Some scattered data exist in the literature on free-radical addition reactions with vinyl- and allyl-silanes. Burkard and Krieble [12] reported the addition of $HSiCl_3$ to trichlorovinylsilane in presence of a peroxide. There were later reports of the addition of trichlorosilane and of dichloromethylsilane to various trialkylvinyl- and dialkyldivinyl-silanes [13, 14]. The additions of halogenated methanes, ethanes, and propanes to vinylsilanes in presence of peroxides have also been carried out [15, 16]. In all these cases the yields of adducts were high, attaining 80%. There is also a reference by Sommer [17] to the addition of butyraldehyde to trimethylvinylsilane in presence of acetyl peroxide, though no information is given about the yield and constants of the adduct. In 1947 Burkard and Krieble [12] reported the addition of $HSiCl_3$ to allyltrichlorosilane, in presence of acetyl peroxide, in 33% yield. There have been no reports about the free-radical addition reactions of 3-butenylsilanes.

We synthesized triethylvinylsilane, allyltriethylsilane, and 3-butenyldiethylmethylsilane by known methods. The reactions were carried out by heating the mixture in presence of benzoyl peroxide. For the addition we used butyraldehyde, benzaldehyde, carbon tetrachloride, and chloroform. The addition of butyraldehyde to triethylvinylsilane went in 60% yield. The reaction went satisfactorily also with benzaldehyde. In this case the yield of adduct was 23%. Good yields were obtained also in the addition of $HCCl_3$ and CCl_4 to triethylvinylsilane in presence of benzoyl peroxide (48% and 43.5%, respectively). The formation of the monomeric product was here accompanied by telomerization products, and a considerable amount of high-boiling substances containing Si and C was obtained.

A series of reactions with carbon tetrachloride, chloroform, butyraldehyde, and methyl formate were carried out with allyltriethylsilane. The reactions were carried out both at atmospheric pressure at 70-100° and under pressure in an autoclave at 150°. In all cases no positive result was obtained; the reactants were generally recovered unchanged. The benzoyl peroxide was converted into benzoic acid. The free-radical reactions with 3-butenyldiethylmethylsilane were carried out under the same conditions as those with triethylvinylsilane, i.e., with heating (80-170°) in presence of benzoyl peroxide at atmospheric pressure.

With benzaldehyde and butyraldehyde we obtained the corresponding ketones in 17 and 27% yield, i.e., in lower yield than in the case of triethylvinylsilane. With carbon tetrachloride and chloroform the corresponding adducts were formed in 78% and 72% yield. A certain amount of high-boiling substances (telomers) was also obtained. The higher yields of the CCl_4 and CHCl_3 adducts for 3-butenyldiethylmethylsilane than for triethylvinylsilane is to be explained by the fact that in the latter case a considerable amount of telomers was obtained, whereas in the former mainly monomer was obtained.

In 1956 Topchiev and co-workers [18] reported addition reactions of HSiCl_3 and of triphenylsilane with various allylsilanes in presence of benzoyl peroxide. It was found that almost no reaction occurs between HSiCl_3 and allyltrimethyl- and allyltriethylsilanes in presence of benzoyl peroxide at 50°; reaction occurs only under severe conditions under pressure at 120°, but in this case the yield of adducts is only 2.5-10%. When the alkyl groups of trialkylallylsilanes are replaced by substituents of electronegative character (phenyl or chlorine), the yields of reaction products rise to 20-60%.

In the free-radical polymerization of 1-, 2-, and 3-alkenylsilanes it was shown also that 2-alkenylsilanes polymerize less readily than 1- and 3-alkenylsilanes [19]. Our results and data in the literature confirm, in our opinion, that a double bond in the β position to silicon is conjugated with the Si-C bond. Allylsilanes have a low tendency to participate in free-radical addition reactions, evidently because the unpaired electron of the free radical formed in the reaction ($\text{R} + \text{C}=\text{C}-\text{C}-\text{Si} \rightarrow \text{R}-\text{C}-\text{C}-\text{C}-\text{Si} \cdot$) is conjugated with the Si-C bond. Such free radicals (those in which the unpaired electron is conjugated) have a high stabilization energy and hence show a reduced tendency to enter into chain propagation [20-22].

The greater success in carrying out the reaction with allyltrichlorosilane leads us to the view that a determining effect on the possibility of the conjugation of the Si-C bond with bonds in the β position is exerted by the character of the other groups or atoms attached to the silicon atom, which determine the electronic structure of the Si-C bond. It may be considered that, if silicon is attached to three chlorine atoms, the Si-C is much less capable of conjugation than if the silicon is attached to three methyl or ethyl groups.

EXPERIMENTAL

Triethylvinylsilane, allyltriethylsilane, and (3-butenyl)-diethylsilane were synthesized by known methods. The carrying out of free-radical addition reactions with triethylvinylsilane is described in [23].

Reaction of Aldehydes with (3-Butenyl)-diethylmethylsilane

A. Butyraldehyde. A mixture of 30 g (0.19 mole) of 3-butenyl-diethylmethylsilane and 49 g (1.18 moles) of butyraldehyde was prepared in a round-bottomed flask fitted with reflux condenser, thermometer, and dropping funnel. The mixture was heated to the boil, and in the course of two hours a solution of 1.5 g of benzoyl peroxide in 49 g (1.18 moles) of butyraldehyde was added dropwise. The mixture was heated at the boil for 50 hours, in the course of which 4.5 g of benzoyl peroxide was added in 0.5-g portions at regular intervals. The boiling point of the mixture rose from 80° to 92°. To remove benzoic acid formed in the reaction, the mixture was washed with sodium carbonate solution and with water. The mixture was dried and fractionated. Fractionation gave 12.2 g of 8-(diethylmethylsilyl)-4-octanone; b.p. 127-128° (3.5 mm); n_D^{20} 1.4470; d_4^{20} 0.8605; found MR 70.79; calculated MR 71.21. The melting point of the 2,4-dinitrophenylhydrazone was 134°. Yield 42% on the 3-butenyldiethylmethylsilane that reacted and 27% on the amount taken. Found: C 68.28; 68.23; H 12.06; 12.20; Si 12.44; 12.26%. $\text{C}_{13}\text{H}_{28}\text{SiO}$. Calculated: C 68.46; H 12.28; Si 12.28%.

B. Benzaldehyde. The reaction was carried out under the same conditions. The amounts taken were 30 g (0.19 mole) of 3-butenyldiethylmethylsilane and 102 g (0.95 mole) of benzaldehyde. The boiling point of the mixture kept in the range 170-180°. Fractionation gave 9.7 g of 5-(diethylmethylsilyl)-valerophenone; b.p. 163-164° (3.5 mm); n_D^{20} 1.5168; d_4^{20} 0.9726; found MR 81.47; calculated MR 82.06. Yield 32% on the 3-butenyldiethylmethylsilane that reacted and 18% on the amount taken. Found: C 73.13; 73.20; H 9.90; 9.86; Si 10.82; 10.94%. $\text{C}_{16}\text{H}_{26}\text{SiO}$. Calculated: C 73.32; H 9.92; Si 10.68%.

Reaction of CCl_4 and of CHCl_3 with (3-Butenyl)-diethylmethylsilane

A. Chloroform. The reaction was carried out under the same conditions. The amounts taken were 30 g (0.19 mole) of 3-butenyldiethylmethylsilane and 136 g (1.14 moles) of chloroform. In the course of 50 hours 5.5 g of benzoyl peroxide was added. The boiling point of the mixture rose from 80° to 95° . Fractionation gave 37.8 g (72%) of diethylmethyl-(5,5,5-trichloropentyl)silane; b.p. $127-129^\circ$ (3 mm); n_D^{20} 1.4647; d_4^{20} 1.0578; found MR 71.86; calculated MR 72.34%; Found: C 43.25; 43.38; H 7.62; 7.42; Si 10.33; 10.14; Cl 37.78; 37.95%, $\text{C}_{10}\text{H}_{21}\text{SiCl}_3$. Calculated: C 43.68; H 7.63; Si 10.15; Cl 38.54%. The yield was 72%.

B. Carbon Tetrachloride. The reaction was carried out under the same conditions. The amounts taken were 30 g (0.19 mole) of 3-butenyldiethylmethylsilane and 176 g (1.14 moles) of carbon tetrachloride. In the course of 50 hours 5.5 g of benzoyl peroxide was added. The boiling point of the mixture rose from 80° to 95° . Fractionation gave 46.3 g (78%) of diethylmethyl-(3,5,5,5-tetrachloropentyl)silane; b.p. $128-130^\circ$ (3.5 mm); n_D^{20} 1.4860; d_4^{20} 1.1684; found MR 76.17; calculated MR 76.68; Found: C 38.46; 38.54; H 6.38; 6.33; Si 9.18; 9.23; Cl 45.20; 45.03%, $\text{C}_{10}\text{H}_{20}\text{SiCl}_4$. Calculated: C 38.70; H 6.46; Si 9.03; Cl 45.81%. The yield was 78%.

SUMMARY

1. Free-radical addition reactions proceed readily with vinyl- and 3-butenyl-silanes, but with difficulty with allylsilanes, which confirms the presence of conjugation between the Si-C bond and a double bond in the β position with respect to silicon.

2. A determining effect on the possibility of conjugation of the Si-C bond is exerted by the character of the other groups or atoms attached to silicon which determine the electron structure of the Si-C bond.

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*Original Russian pagination. See C.B. Translation.

RAMAN SPECTRUM METHOD FOR THE INVESTIGATION OF HYDROCARBONS

COMMUNICATION 12. RAMAN SPECTRA OF SOME HYDROCARBONS OF VARIOUS CLASSES

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Khimicheskikh Nauk*, No. 1, pp. 84-89, January 1960
Original article submitted May 30, 1958

In the present paper we give the Raman spectra of seven hydrocarbons belonging to various homologous series. These substances were synthesized and studied in connection with the solution of various problems arising in the course of our work in the laboratory and not specially for the present series of investigations. Although the spectra of these hydrocarbons have been published in a special monograph [1], we considered it desirable to give our results here since the monograph gave only the spectroscopic data and gave no information about the methods of preparation and purification of the substances and no discussion of the individual spectra. The spectra of the hydrocarbons studied, with the exception of 1,1,2-trimethylcyclopropane and 1-ethyl-2-methylcyclohexene, are of interest in the analysis of ligoins by the combined method [2, 3].

EXPERIMENTAL

The procedure for the determination and measurement of the spectra was described previously [4, 5].

Dodecane was prepared from hexyl alcohol (purified by distillation through a column) via hexyl bromide by the Wurtz method; it was vacuum-distilled through a column of about 80-plate efficiency; b.p. 114.0-114.1° (27.5 mm); n_D^{20} 1.4221; d_4^{20} 0.7492. The literature [6] gives: b.p. 216.278° (760 mm); n_D^{20} 1.42160; d_4^{20} 0.74869.

$\Delta\nu$: 234(1,w), 252(0), 264(3,w), 302(2,w), 345(1,w), 400(1,w), 505(0), 529(0), 590(1,w), 701(0), 715(0), 726(0), 761(0), 781(1,w), 804(1,w), 837(7,w), 846(7,w), 870(5,w), 892(11,w), 920(2), 962(5,w), 985(0), 1004(0), 1026(7,w), 1041(3,w), 1062(14), 1081(20), 1096(2), 1133(13), 1162(1), 1196(2,w), 1243(3), 1274(2,w), 1301(35), 1438(55,w), 1456(50,w), 2853(160,w, ϕ), 2879(170,w), 2892(170,w, ϕ), 2936(80,w, ϕ), 2962(70, ϕ).

5,5-Dimethylundecane was prepared from distilled hexyl alcohol via hexyl bromide, which was converted by Grignard reaction with acetone into 2-methyl-2-octanol; by the action of dry hydrogen chloride the latter was converted into 2-chloro-2-methyloctane, which by reaction with butylmagnesium bromide in presence of mercuric chloride was converted into 5,5-dimethylundecane. The hydrocarbon was purified by chromatography on silica gel and was then vacuum distilled through a column of 25-plate efficiency; b.p. 101.0° (16 mm); n_D^{20} 1.4272; d_4^{20} 0.7601. It was synthesized for the first time [7].

*Key: w, broad; ϕ , background; Δ , doublet; n polarized (at least partially); p sharp.

Δv : 222(1), 247(6,w), 269(1), 293(1), 308(12, w), 335(3, w), 372(1,w), 407(1,w), 445(1), 466(8,w), 494(3,w), 515(0), 553(3), 599(0), 713(0), 731(1, w), 757(8,w), 790(3,w), 806(1,w), 814(3), 845(3), 859(1), 878(13), 894(14), 911(11), 935(7), 971(3,w), 986(1), 1004(3), 1029(4), 1051(1), 1064(16), 1074(3,w), 1088(1,w), 1118(10,w), 1151(0), 1172(3), 1185(9), 1199(11), 1214(3), 1243(6), 1268(4), 1283(1), 1305(22,w), 1342(5), 1363(5), 1440(55), 1456(30), 1467(15), 2849(80), 2858(80), 2873(80), 2894(150), 2908(100), 2936(60), 2962(100).

1,1,2-Trimethylcyclopropane was prepared from mesityl oxide by the Kizhner reaction via 3,5,5-trimethylpyrazoline [8] and was distilled through a column of 40-plate efficiency; b.p. 53.1° (760 mm); n_D^{20} 1.3862; d_4^{20} 0.6948. According to literature data [9]; b.p. 52.55° (760 mm); n_D^{20} 1.3864; d_4^{20} 0.6947.

Δv : 208(0), 235(1), 266(1,w), 313(1,w), 363(25), 376(25), 446(17), 464(9), 678(80,n), 757(75,n), 788(1), 863(28,n), 888(55,n), 906(5), 926(1), 941(1), 959(5), 982(8), 996(7), 1020(7), 1036(1), 1100(15), 1113(28,n), 1127(24), 1142(0), 1164(6), 1204(0), 1258(11), 1308(30), 1369(16,n), 1393(25,n), 1448(36), 1460(44), 1471(5), 2833(0), 2869(100,n), 2889(10), 2908(10), 2926(95,n), 2950(70), 2964(5), 2992(140,n).

sec-Butylcyclopentane was prepared by the condensation of cyclopentadiene with 2-butanone with formation of 6-ethyl-6-methylfulvene, which was then hydrogenated in an autoclave at room temperature [10]. The hydrocarbon obtained was treated chromatographically on silica gel and distilled through a column of 40-plate efficiency; b.p. 153.5° (760 mm); n_D^{20} 1.4356; d_4^{20} 0.7951. The literature [11] gives: b.p. 154.4° (760 mm); n_D^{20} 1.4357; d_4^{20} 0.7945.

Δv : 331(23,w), 346(3), 383(4,w), 407(3), 429(3,w,φ), 482(6), 508(5), 530(1), 718(0), 745(1), 770(3,w), 807(4,φ), 823(2), 834(7, w), 862(3, w), 897(31), 935(5 w, φ), 951(5 w, φ), 970(0), 982(2), 996(4,w), 1011(0), 1029(22,w), 1038(15), 1092(4,w), 1105(3,w), 1138(8,w), 1155(9), 1169(2), 1192(10,w), 1231(0), 1252(0), 1279(5,φ), 1290(4), 1308(6,φ), 1324(5), 1342(4), 1361(7,φ), 1447(65,w), 1461(10,φ), 2856(130,w,φ), 2873(160,w,φ), 2911(130,φ), 2936(160,φ), 2965(170,w,φ).

2-Cyclopentyl-octane was prepared from cyclopentadiene and 2-octanone via 6-hexyl-6-methylfulvene; the last compound was hydrogenated at room temperature and 110 atm in presence of a nickel catalyst. The hydrocarbon was then treated chromatographically on silica gel and vacuum distilled through a column of 40-plate efficiency; b.p. 120.5° (19 mm); n_D^{20} 1.4475; d_4^{20} 0.8118. It was synthesized for the first time [7].

Δv : 229(3,w), 252(6,w), 266(0,w), 322(0,w), 334(0), 363(0), 408(3), 517(0,w), 703(0), 721(0), 760(0,w), 790(0), 803(1), 815(0), 840(6), 857(4), 866(4), 880(2), 896(25), 955(1), 975(6), 1028(13), 1041(13), 1063(6), 1076(16), 1098(6,w), 1135(16), 1154(3), 1174(3), 1198(3), 1222(1), 1241(0), 1251(0), 1271(0), 1290(0), 1302(20), 1329(4), 1362(4), 1388(3), 1436(40), 1447(60), 1459(20), 2850(180), 2872(190), 2891(80), 2907(80), 2936(100), 2960(120).

Propylcyclohexane was prepared from propylbromide and cyclohexanone by the Grignard method via 1-propylcyclohexanol; the last compound was vacuum distilled through a column of 20-plate efficiency and dehydrated with oxalic acid; the propylcyclohexene was hydrogenated at atmospheric pressure and room temperature in presence of platinized charcoal activated with chloroplatinic acid [12]. The propylcyclohexane was distilled through a column of 80-plate efficiency; b.p. 157.1° (760 mm); n_D^{20} 1.4372; d_4^{20} 0.7936. The literature [6] gives: b.p. 156.724° (760 mm); n_D^{20} 1.43705; d_4^{20} 0.79360.

Δv : 272(0), 298(29), 314(0,w), 329(0,w), 355(0), 400(0,w), 430(0), 444(20), 465(0,w), 475(0,w), 500(0), 532(1,w), 542(2), 566(2), 587(0), 738(8), 768(3), 781(37), 787(37), 794(19), 825(0,w), 842(16), 869(5), 882(8), 898(8), 921(1), 953(4), 967(6), 1020(9), 1032(65), 1054(14), 1087(9), 1102(13), 1110(13), 1152(4), 1161(15), 1189(9), 1213(1), 1235(0), 1253(25), 1263(36), 1275(17), 1293(15), 1309(0), 1333(0), 1346(17), 1365(12), 1443(80), 1459(14), 2843(240,n), 2851(240,n), 2871(120), 2891(120), 2916(230), 2936(230), 2960(70).

1-Ethyl-2-Methylcyclohexene was prepared by the Grignard reaction from ethylmagnesium bromide and 2-methylcyclohexanone, purified by repeated crystallization from ether at low temperature and by distillation through a column of 20-plate efficiency, via 1-ethyl-2-methylcyclohexanol. The last compound was dehydrated by the action of oxalic acid, and the unsaturated hydrocarbon was fractionated through a column of 100-plate efficiency having a copper filling. For the spectroscopic investigation we took the main fraction*; b.p. 78.0° (56 mm); n_D^{20} 1.4634; d_4^{20} 0.8297. The literature [13] gives: 156.7–157.0° (760 mm); n_D^{20} 1.4630; d_{20}^{20} 0.832.

Δv : 203(1), 215(1), 233(5,w), 259(5), 272(8), 290(3), 308(10), 345(6,w), 360(6), 399(3), 413(3), 444(17), 454(15), 477(13), 489(2), 554(17), 565(4), 591(6), 628(3), 666(40,p), 675(42,p), 717(3), 728(1), 748(2), 776(1), 799(0), 820(12), 832(2), 844(8), 860(1), 873(17,p), 891(2), 922(6), 960(18), 997(15), 1010(1), 1031(14), 1052(23,p), 1075(14), 1086(19), 1105(1), 1143(8,w), 1178(30,p), 1195(0), 1217(5), 1246(2), 1262(3), 1272(25,w), 1321(8,w), 1327(6), 1338(8), 1356(15), 1377(19,w), 1430(100,p), 1448(70,w), 1458(65,w), 1643(3), 1673(95,w), 2832(120,w), 2862(200,w,φ), 2870(180,w,φ), 2903(210,w,φ), 2915(100,φ), 2935(220,w,φ), 2963(100,w), 2986(10).

* This contained a slight admixture of isomers with the double bond in other positions (see next page).

DISCUSSION OF RESULTS

Dodecane. The spectrum of this hydrocarbon is given in the literature [14, 15]. Comparison with Goubeau's results [14], which were obtained by photographic-recording methods, shows that we recorded many more lines, probably because of better conditions of resolution. As in the spectra of other *n*-paraffins, relatively bright lines at 1133 and 1301 cm^{-1} , typical for this class of compound, were observed [16].

5,5-Dimethylundecane. The spectrum of 5,5-dimethylundecane was determined for the first time; it contains a line at 757 cm^{-1} , which is characteristic for a quaternary carbon atom [16] and also bright lines in the regions 900-940 and 1200-1270 cm^{-1} .

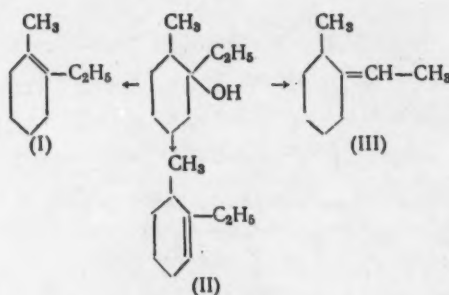
1,1,2-Trimethylcyclopropane. Comparison of the spectrum of 1,1,2-trimethylcyclopropane with those of the known monoalkylcyclopropanes shows that the bright polarized line of the fully symmetrical vibration of the ring at about 1200 cm^{-1} [17-19] is practically absent. Analogous phenomena of the disappearance or sharp change in the frequency of lines of the fully symmetrical vibration of the unsubstituted ring is observed also in the spectra of other monocyclic and aromatic hydrocarbons with the introduction of two or more substituents [19]. It is probable that the interaction of more than one substituent with the ring results in a substantial change in the field of force of the latter and therefore its characteristic spectrum. It is also of note that lines in the region 3050-3080 cm^{-1} , characteristic of the spectra of the monoalkylcyclopropanes studied [20], are absent.

sec-Butylcyclopentane and 2-Cyclopentyl-octane. In the spectra of these (the spectrum of the second was determined for the first time) we observed a line due to the fully symmetrical vibration of the five-membered ring at about 890 cm^{-1} [21]; the intensity of this falls with rise in molecular weight.

Examination of the spectra of the two paraffin and two cyclopentane hydrocarbons shows that there is also a general reduction in the intensities of the lines of lower frequency (up to 750 cm^{-1}) and an increase in their diffuseness as the molecular weight increases. Both of these effects are known to be associated with increase in the number of possible rotation isomers in the open-chain sections. Actually, the main differences in the vibration spectra of rotation isomers appear in the region of γ -frequencies [22].

Propylcyclohexane. The spectrum of this hydrocarbon contains a series of bright lines characteristic of monoalkylcyclohexanes [23]: 444(20), 842(15), 1032(65), 1054(14), 1161(15), 1253(25), 1263(36), 1346(17), 1365(12). It is of interest also to note the presence of a sharp doublet at 781-787 cm^{-1} , which is readily resolved when the spectrograph slit is narrowed to a distance corresponding to 2 cm^{-1} in the spectrum.

1-Ethyl-2-methylcyclohexane. The spectrum of this compound, which was determined for the first time, requires special consideration. First of all, it must be acknowledged that the position of the double bond in our hydrocarbon was not rigorously proved. In the course of its synthesis, in the dehydration of the intermediately formed 1-ethyl-2-methylcyclohexanol, three structural isomers could arise:



It was by this method that Signalgo and Cramer [13] prepared the substance to which they attributed the structure (I). The purity of their preparation was probably not very high, because in the distillation they used only a column with a spiral tube, 51 cm in height; a column of this type is not very efficient: of not more than 5-6 theoretical plates [24].

We prepared 1-ethyl-2-methylcyclohexene by the same scheme with the exception that we used oxalic acid instead of iodine for the dehydration of 1-ethyl-2-methylcyclohexanol. Although we distilled our preparation through a much more efficient column, the two preparations had extremely close constants:

	n_D^{20}	d_4^{20}
Signaigo and Cramer's preparation	1.4630	0.830*
Our preparation	1.4634	0.8297

This permits us to suppose that all the conclusions reached regarding the structure of our preparation will apply also to Signaigo and Cramer's preparation.

Signaigo and Cramer did not try to establish the position of the double bond in their product, but assigned it the structure (I) on the grounds that Wallach [25] in the dehydration of 1,2-dimethylcyclohexanol with a drop of sulfuric acid obtained 1,2-dimethylcyclohexene, which he proved had a structure analogous to (I) by the method of decomposition of chloro nitroso compounds. However, conclusions reached for the first member of a series cannot always be extended to the succeeding members. It must be granted that Signaigo and Cramer's view is supported by the fact that, in the dehydration of tertiary alcohols of the cyclohexane series, hydrocarbons in which a group is double-bonded to the ring [structure (III)] are obtained with great difficulty. Thus, in the case of monoalkylcyclohexanols Wallach was quite unable to detect them, and Mosher [26] showed that, from the corresponding alcohols, methylenecyclohexane is not formed at all, the yield of ethylenecyclohexane is less than 1%, and even in the case of isopropylidenecyclohexane the yield is only about 5%.

Hence, the preparations obtained by Signaigo and Cramer and by us cannot have the structure (III), but the structure (II) cannot be regarded as finally excluded. It might be feared that these preparations are mixtures of closely boiling hydrocarbons of structures (I) and (II). However, an examination of the spectroscopic data enables us to exclude structure (II). If (II) were present we should be able to observe a line in the 3000-3100 cm^{-1} region corresponding to the valence vibrations of a CH group at a double bond. However, no such line is observed in the spectrum. Hence, there is no hydrogen atom at the double bond of our hydrocarbon, which is possible only in the structure (I).

It must be pointed out that in the region of the valence vibrations of the C-C group, apart from the intense line at 1673 cm^{-1} which belongs to 1-ethyl-2-methylcyclohexene, there is also a weak line at 1643 cm^{-1} , which corresponds to 1-alkenes and is probably due to a small amount (3-5%) of 1-methyl-2-vinylcyclohexane impurity; the origin of this is obscure. It will be obvious that the spectrum of the 1-methyl-2-vinylcyclohexane impurity will doubtless contain lines in the region 3000-3100 cm^{-1} , but we did not observe these because the amount of this impurity was too small.

SUMMARY

1. The Raman spectra of seven hydrocarbons of various structures were determined.
2. By a consideration of chemical and spectroscopic data it was confirmed that, in the dehydration of 1,2-dialkylcyclohexanols, o-dialkylcyclohexenes are obtained in which the double bond is predominantly in the position shown in structure (I).

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CATALYTIC TRANSFORMATIONS OF p-CYMENE
OVER PLATINIZED ALUMINA IN PRESENCE
OF HYDROGEN UNDER PRESSURE

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Translated from *Izvestiya Akademii Nauk SSSR, Otdelenie
Khimicheskikh Nauk* No. 1, pp. 90-93, January, 1960

Original article submitted June 6, 1958

Several investigations have been devoted to the transformations of aromatic hydrocarbons at high temperature under high pressures of hydrogen [1-6]. Thus, Haensel and Donaldson [1] in the passage of cumene over a platinum catalyst at 459° and 35 atm, found that the catalyzate contained trimethylbenzenes (13.7%), ethyltoluenes (8.4%), and benzene (19%). Shuikin and Berdnikova [2], who investigated the transformations of benzene, toluene, and ethylbenzene over platinized alumina at 450° and 20 atm, showed that the catalyzates contained pentane, isopentane, cyclohexane, methylcyclopentane, toluene, xylenes, biphenyl, and naphthalene. In a study of the transformations of propyl-, isopropyl-, and butyl-benzenes over a nickel-alumina catalyst [3, 4] at 350-405° and hydrogen pressures of 25 and 50 atm, the same authors found that these hydrocarbons mainly undergo dealkylation and disproportionation of side groups and that the rate of transformation of these alkylbenzenes depends not only on the nature of the catalyst, but also on the length of the side chain. Pitts and co-workers [6] described the isomerization of a mixture of xylenes, ethylbenzene, and cumene over a platinized aluminum silicate under the conditions of catalytic reforming. They considered that the isomerization of these compounds proceeds through the intermediate formation of cyclohexane hydrocarbons.

In a previously published investigation [7] we showed that at 450° and 520° under 20 atm of hydrogen, in presence of platinum-alumina, 1-isopropyl-4-methylcyclohexane undergoes not only dehydrogenation to p-cymene, but also dealkylation with formation of toluene, xylenes, and ethyltoluenes. Under these conditions dehydroisomerization into ethylxylenes also occurred to a considerable extent. In the further development of the earlier investigation it was considered interesting to study the behavior of p-cymene, as one of the products of the catalytic transformations of 1-isopropyl-4-methylcyclohexane. It was found that p-cymene undergoes dealkylation much more readily than 1-isopropyl-4-methylcyclohexane. As well as the rupture of the C_{ar}-C_{al} link, hydrogenolysis of the C-C links of the side chains occurred with formation of the lower homologs of benzene and of benzene itself.

EXPERIMENTAL

After being redistilled through a column of 70-plate efficiency the p-cymene had the following properties: b.p. 177.2° (760 mm); n_D^{20} 1.4909; d_4^{20} 0.8573. The transformations of p-cymene were investigated in a flow system in presence of a platinum-alumina catalyst containing 0.5% of platinum at 450° and 520° under a pressure of 20 atm at a space velocity of 0.5 hour⁻¹. The properties of the catalyzates and the gas compositions are presented in Tables 1, 2, and 3. The catalyzates were fractionated through a column. The fractions were characterized by their physical constants, and their compositions were determined by chemical methods or by the determination of the Raman spectrum.

TABLE 1

Properties of p-Cymene Catalyzates Obtained in Presence of 0.5% Pt-Al₂O₃

Expt.	Temp. of expt. (°C)	Pressure (atm)	Amount of hydrocarbon taken (g)	Yield of catalyzate (% by wt)	n_D^{20}	Composition of gas (%)			
						H ₂	CH ₄	C ₂ H ₆	C ₃ H ₈
1	450	20	85,7	73,6	1,4876	72,4	19,8	2,4	5,4
2	520	20	88,1	72,7	1,4926	72,9	6,7	9,3	11,1

TABLE 2

Fractional Composition of p-Cymene Catalyzate Obtained at 450° and 20 atm

Fraction	B.p. (°C at 747 mm)	n_D^{20}	d_4^{20}	Yield of fraction (% by wt)	
				on original hydrocarbon	on catalyzate
I	65,0—101,0	1,4495	0,7956	3,4	4,6
II	101,0—110,6	1,4535	0,7957	1,5	2,0
III	110,6—110,8	1,4965	0,8675	22,9	30,9
IV	110,8—150	1,4894	0,8582	3,1	4,3
V	150—175,8	1,4830	0,8482	8,6	11,7
VI	175,8—176	1,4895	0,8567	14,2	19,3
VII	176—177,5	1,4915	0,8578	11,2	15,6
VIII	177,5—179	1,4928	0,8616	1,8	2,5
Residue				2,7	3,6

TABLE 3

Fractional Composition of p-Cymene Catalyzate Obtained at 520° and 20 atm in Presence of 0.5% Pt-Al₂O₃

Fraction	B.p. (°C at 747 mm)	n_D^{20}	d_4^{20}	Yield of fraction (% by wt. on catalyzate)
I	79—79,2	1,4820	0,8583	3,9
II	79,2—110,2	1,4894	—	2,0
III	110,2—110,5	1,4962	0,8672	47,0
IV	110,5—135	1,4960	0,8654	1,5
V	135—144,2	1,4961	0,8624	4,1
VI	144,2—153,6	1,4947	—	1,1
VII	153,6—170	1,4952	0,8621	6,9
VIII	170—175,5	1,4920	0,8592	1,7
IX	177,5—177,2	1,4907	0,8571	14,9
X	177,2—186	1,4948	0,8620	8,1
Residue				4,7

Fractions I and II (Table 2) were combined and subjected to chromatographic adsorption on silica gel. We isolated 1.2 g of a substance of b.p. 79.5–110.5° (752 mm) and n_D^{20} 1.4984, which was found to be a mixture of benzene and toluene. The naphthene-paraffin part of these two fractions of the catalyzate (1.8 g), b.p. 65–102° (752 mm) and n_D^{20} 1.4072, was subjected to Raman-spectrum analysis; it was found that it contained methylcyclohexane, cyclopentane hydrocarbons, and paraffins. Fraction III consisted of toluene. Ullmann oxidation of this gave benzoic acid, m.p. 121.2°.

Fraction IV was oxidized with permanganate. Following the method proposed by Moldavskii and co-workers [8] from the oxidation products we isolated benzoic acid (m.p. 121°), phthalic acid (m.p. 190°), isophthalic acid (m.p. of dimethyl ester 65°), and terephthalic acid (m.p. of dimethyl ester 140°). Raman-spectrum analysis showed that Fraction V contained about 45% of p-ethyltoluene, about 15% of o-ethyltoluene, about 10% of m-ethyltoluene, and about 30% of cumene.

Fractions VI and VII were unchanged p-cymene. The residue (2.3 g) boiled over the range 179-194° and had n_D^{20} 1.5024. It probably consisted mainly of a mixture of ethylxylenes.

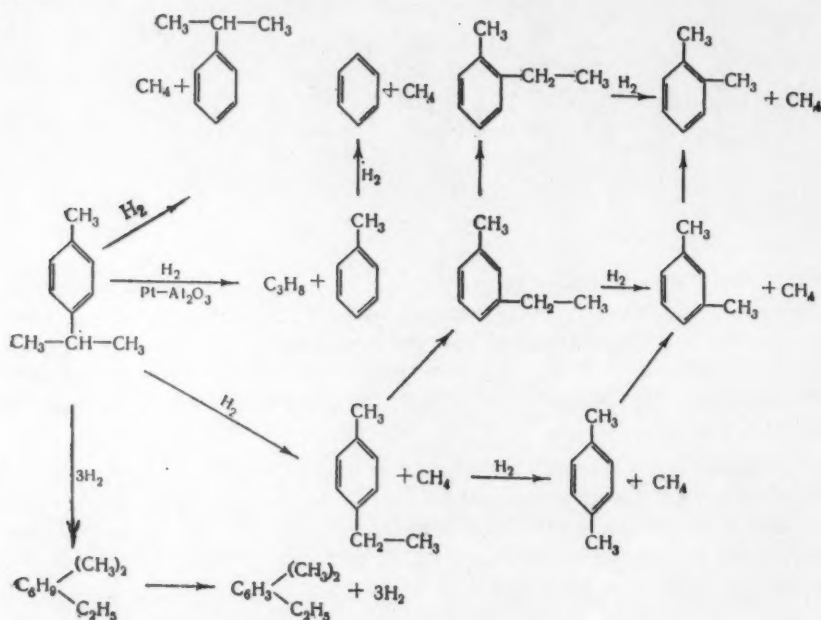
Table 3 shows that Fraction I contained much benzene. After chromatographic separation of impurities on silica gel it had the following properties: b.p. 80.0° (754 mm); n_D^{20} 1.5010; d_4^{20} 0.8794.

Fraction III was pure toluene. Fraction V contained a mixture of xylenes. From the Raman spectra of combined Fractions VI and VII it was shown that they consisted of a mixture of ethyltoluenes. Fraction IX was p-cymene. It was shown by spectrum analysis that Fraction X consisted of a mixture of ethylxylenes. The residue (2.6 g) boiled over the range 186-232° (745 mm) and had n_D^{20} 1.5107; it probably consisted of a mixture of polyalkylbenzenes.

Hence, Tables 2 and 3 show that the bulk of the catalyzate obtained in presence of platinized alumina consists of toluene, xylenes, ethyltoluenes, and ethylxylenes. The experiments show that p-cymene is more readily dealkylated than 1-isopropyl-4-methylcyclohexane. The yield of dealkylation products of p-cymene treated at 450° and 520° were 48% and 64%, respectively, whereas the yields obtained from 1-isopropyl-4-methylcyclohexane were about 30% and about 50%.

It should be noted that under the given conditions, the main reaction is the rupture of an energetically strong bond uniting the aliphatic chain to the aromatic nucleus. The $C_{ar}-C_{al}$ bond energies in cumene and toluene are 83 and 87.5 kcal/mole, respectively, and the $C_{al}-C_{al}$ bond energy in p-cymene is 60 kcal/mole [9]. Hence, the use of a catalyst and of high pressure probably changes the relative stabilities of various bonds, and we cannot exclude the view that the determining factor is the nature of the catalyst. However, under the conditions of high temperature and hydrogen pressure, in addition to rupture of $C_{ar}-C_{al}$ bonds there occurs the hydrogenolysis of carbon-carbon bonds of the p-cymene side chain with formation of p-ethyltoluene and p-xylene. On the surface of the catalyst these compounds probably undergo disproportionation of side chains with formation of m- and o-ethyltoluenes and other xylenes.

In the catalytic transformations of p-cymene the catalyzate contained 3.6-8.1% of ethylxylenes. The formation of these can be regarded as due to the alkylation of ethyltoluenes by breakdown products or to the isomerization of alkyl radicals in the original hydrocarbon. The fact that the yield of ethylxylenes does not rise with rise in the ethyltoluene content of the catalyzate, and also that preliminary hydrogenation of p-cymene to 1-isopropyl-4-methylcyclohexane facilitates the isomerization of side groups [8], gives us grounds for the view that the disproportionation reaction proceeds in the cyclohexane hydrocarbon molecule, so that cyclohexanes are intermediate products in the formation of ethylxylenes. These views are in accord with Pitts's investigations [6] on the isomerization of ethylbenzene and cumene. Our results enable us to represent the transformations of p-cymene as follows:



SUMMARY

1. A study was made of the catalytic transformations of p-cymene in presence of platinized alumina at 450° and 520° under a hydrogen pressure of 20 atm.

2. With rise in temperature from 450° to 520° the conversion of this hydrocarbon rises from 48% to 64%; in both cases the hydrogenolysis of C_{ar}-C_{al} and C_{al}-C_{al} bonds occurs.

3. Under the given conditions the main transformation of p-cymene consists in the dealkylation of side chains with formation of ethyltoluenes, xylenes, toluene, and benzene, and also the redistribution of radicals with formation of ethylxylenes.

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ALKYLATION OF AROMATIC HYDROCARBONS
WITH CYCLOHEXENE IN PRESENCE OF
 $(C_2H_5)_2AlBr \cdot C_2H_5AlBr_2$

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and G. I. Nikishin

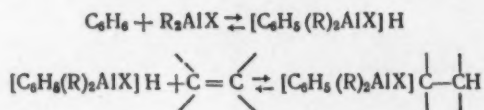
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Translated from *Izvestiya Akademii Nauk SSSR, Otdelenie*

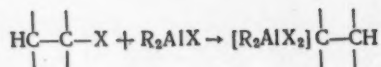
Khimicheskikh Nauk, No. 1, pp. 94-97, January 1960

Original article submitted December 19, 1958

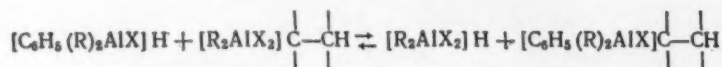
Organoaluminum compounds have recently begun to receive wide application as initiators for the polymerization of ethylene and propene at low pressures. In the present investigation we studied the application of ethylaluminum bromides as catalysts for the alkylation of monocyclic aromatic hydrocarbons with cyclohexene with the object of obtaining mono- and di-cyclohexyl derivatives. The synthesis of cyclohexylbenzenes is of interest from the point of view of finding the conditions for the alkylation of aromatic hydrocarbons with olefins in presence of the new catalyst. The catalyst which we used, an equimolecular mixture of diethylaluminum bromide and ethylaluminum dibromide, was prepared from aluminum and ethyl bromide. The mechanism of alkylation with this catalyst is clearly analogous to that of the alkylation of aromatic hydrocarbons with olefins in presence of aluminum chloride. The organoaluminum compound (diethylaluminum bromide or ethylaluminum dibromide) forms an intermediate complex with the aromatic hydrocarbon, and to this the olefin adds:



This ternary complex decomposes with formation of the alkylbenzene and R_2AlX . It may be supposed also that olefin combines with hydrogen bromide formed by the hydrolysis of ethylaluminum bromides and the product then reacts with the catalyst:



The complexes present in the reaction mixture undergo an exchange reaction:



The newly formed complexes decompose with liberation of the alkylbenzene, R_2AlX , and HX :

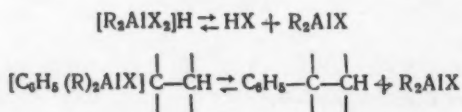


TABLE 1

Alkylation products	Toluene: cyclohexene molar ratio		
	1:1	1:1.2	1:1.5
Monocyclohexyltoluene	26	21	22
Dicyclohexyltoluene	14	20	37
Polycyclohexyltoluenes	19	29	40

TABLE 2

Aromatic hydrocarbon	Yield of alkylation product	Yield of monoalkylated product (%)		Yield of dialkylated product (%)		Yield of polyalkylated product (%)		Intermediate fractions (%)	
		on original reactants	on alkylation product	on original reactants	on alkylation product	on original reactants	on alkylation product	on original product	on alkylation reactants
Toluene	69	26	33	14	18	19	24	10	25
o-Xylene	68	42	58	6	8	13	17	7	17
m-Xylene	72	40	52	12	16	15	20	5	12
p-Xylene	61	18	28	17	26	19	29	7	17

TABLE 3

Aromatic hydrocarbon	Molar ratio of reactants	Consumption (%)	
		cyclohexene	aromatic hydrocarbon
Toluene	1:1	100	69
o-Xylene	1:1	98	68
m-Xylene	1:1	100	72
p-Xylene	1:1	100	71

Our catalyst has several advantages over aluminum chloride: It is much more soluble in aromatic hydrocarbons, it is readily measured out, and the amount required is smaller for given amounts of reactants. Thus, in all the experiments we used 0.01 mole of catalyst per mole of cyclohexene and obtained a satisfactory yield of alkylation product, whereas other authors [1, 2] who worked with aluminum chloride, used 0.12-0.3 mole of aluminum chloride per mole of cyclohexene. At a benzene: cyclohexene molar ratio of 1:1.5 we obtained mono- and di-cyclohexylbenzenes in a total yield of 53.3%. Corson and Ipatieff [2] with a benzene: cyclohexene: AlCl_3 molar relationship of 1:1.3:0.19 (reaction temperature 3-18°) obtained mainly 1,3,5-tricyclohexylbenzene, and appreciably less (21%) of mono- and di-cyclohexylbenzenes; with a relationship of 1:2:0.22, not only tricyclohexylbenzene, but also a large amount of tetracyclohexylbenzene was formed, and the yield of mono- and di-alkylbenzenes was reduced to about 11%. Beery [3], who alkylated benzene with cyclohexene at a benzene: cyclohexene: AlCl_3 molar relationship of 1.05:1:0.13, obtained cyclohexylbenzene in a yield of only 9.6% together with a large amount of high-boiling products.

We studied the alkylation process for a series of hydrocarbons: benzene, toluene, and o-, m-, and p-xylenes. The choice of these hydrocarbons was determined by the desire to study both the possibilities of the new catalyst and also the effect of the number and positions of the alkyl groups on the yield of mono- and di-cyclohexyl derivatives.

EXPERIMENTAL

In all the experiments the catalyst was prepared in the reaction flask in an amount of 0.01 mole (calculated from the amount of aluminum taken) per mole of cyclohexene. The reaction was carried out in an atmosphere of a dry inert gas. In order to activate the aluminum powder, a small amount of allyl bromide was added, and

when reaction had started the calculated amount of ethyl bromide was added. When the ethyl bromide had reacted, the aromatic hydrocarbon was introduced and the catalyst dissolved. The contents of the flask were heated to about 70°, and the calculated amount of cyclohexene was added in portions; the temperature then rose to 100-120°. When the addition of cyclohexene was complete, the reaction mixture was heated further for four hours at 80-85°, and was then decomposed with water and dried over calcium chloride; the unchanged components of the mixture were distilled off, and the residue was fractionally distilled.

The cyclohexene used in the reactions was obtained from cyclohexanol by dehydration over phosphoric acid. The amount of aromatic hydrocarbon taken for reaction was not less than one mole.

Alkylation of Benzene. The benzene : cyclohexene molar ratio was 1 : 1.5. The yield of alkylation product was 76.5%, and the yield of cyclohexylbenzene [phenylcyclohexane] was 20%, calculated on the original reactants, and 26% on the alkylation product; b.p. 102-103° (1 mm); d_4^{20} 0.9391; n_D^{20} 1.5235. Found: MR 52.16; Calculated: MR 52.13. The literature [1, 2] gives: b.p. 240-243°; d_{16} 0.947; n_D^{16} 1.527; b.p. 238.6-138.8°; d_4^{20} 0.944; n_D^{20} 1.5254. The yield of dicyclohexylbenzene was 33.3% on the original reactants and 43% on the alkylation product; b.p. 140-141° (1 mm); d_4^{20} 0.9643; n_D^{20} 1.5355; found MR 78.32; calculated MR 77.80. The product solidified completely at 17°. The literature [2] gives: b.p. 335-340° (756 mm); d_4^{20} 0.966; n_D^{20} 1.5357.

Alkylation of Toluene. The molar proportions of the reactants and the yields of mono-, di, and poly-alkyl products are presented in Table 1.

Table 1 shows that with increase in the amount of cyclohexene taken for reaction the yield of di- and poly-alkylated products increases. The products isolated had the following properties: Cyclohexyltoluene: b.p. 103-104° (1.5 mm); d_4^{20} 0.9354; n_D^{20} 1.5245; found MR 56.72; calculated MR 56.78. The literature [4, 1] gives: b.p. 254-260° (715 mm); d_4^{20} 0.9343; n_D^{20} 1.5250; b.p. 255-261°; d_{16} 0.938; n_D^{16} 1.5270. Dicyclohexyltoluene: b.p. 154-156° (1 mm); d_4^{20} 0.9614; n_D^{20} 1.5365; found MR 83.23; calculated MR 82.45. The literature [5] gives: b.p. 165-166° (3 mm); d_4^{20} 0.9645; n_D^{20} 1.5378.

Alkylation of o-Xylene. The o-xylene : cyclohexene molar ratio was 1 : 1; the yields of alkylation products are given in Table 2. The cyclohexyl derivatives of o-xylene, which were isolated from the reaction mixture by distillation, had the following properties: Cyclohexyl-o-xylene: b.p. 101-103° (2 mm); d_4^{20} 0.9352; n_D^{20} 1.5275; found MR 61.94; calculated MR 61.43. Found: C 89.42; 89.18; H 11.11; 11.12% $C_{14}H_{20}$. Calculated: C 89.36; H 10.63%.

Alkylation of m-Xylene. The m-xylene : cyclohexene molar ratio was 1 : 1; the yields of products are given in Table 2. Properties of products isolated: Cyclohexyl-m-xylene: b.p. 104-106° (3 mm); d_4^{20} 0.9302; n_D^{20} 1.5245; found MR 61.98; calculated MR 61.43. The literature [1] gives: b.p. 266-268 (763 mm); d_{16} 0.931; n_D^{16} 1.525. Dicyclohexyl-m-xylene: b.p. 165-167° (1 mm); m.p. 78°; this is probably 4,6-dicyclohexyl-m-xylene.

Alkylation of p-Xylene. The p-xylene : cyclohexene molar ratio was 1 : 1; the yields of products are given in Table 2. Properties of products isolated: Cyclohexyl-p-xylene: b.p. 107-108° (3 mm); d_4^{20} 0.9345; n_D^{20} 1.5255. found MR 61.79, calculated MR 61.43. Dicyclohexyl-p-xylene: b.p. 185-187° (1 mm); m.p. 130°. After several crystallizations from alcohol Boudroux [1] isolated a dicyclohexyl-p-xylene of m.p. 156-157°. The difference in melting point between our product and that of Boudroux is to be explained by the fact that on crystallization the symmetrical isomer separates, and this has the higher melting point.

Table 3 gives results on the consumption of the hydrocarbons (mole percent) in the alkylation reaction at a catalyst: cyclohexene molar ratio of 1 : 100.

The cyclohexene reacts completely, and the aromatic hydrocarbons react to the extent of 60-70%. Table 2 shows that under given reaction conditions the greatest yields of monoalkylated products are given by o- and m-xylenes. The yields of monoalkylated products fall in the series o-xylene > m-xylene > toluene > p-xylene; the yields of di- and poly-alkylated products rise in this series: o-xylene < m-xylene < toluene < p-xylene

SUMMARY

1. Ethylaluminum bromides are more active catalysts than aluminum chloride for the alkylation of aromatic hydrocarbons with cyclohexene.

2. Along the series o-xylene, m-xylene, toluene, p-xylene the yield of monocyclohexyl derivative diminishes and the yield of di- and poly-cyclohexyl derivatives increases.

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RELATION OF REACTIVITY TO STRUCTURE FOR ALKENES,
ACID ANHYDRIDES, AND ACID CHLORIDES

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Translated from *Izvestiya Akademii Nauk SSSR, Otdelenie*

Khimicheskikh Nauk 1960, No. 1, pp. 98-103, January 1960

Original article submitted May 26, 1958

The reaction of alkenes with monocarboxylic anhydrides and acid chlorides and with the acid chlorides of monoethyl esters of dicarboxylic acids in presence of metal halides permits the preparation of α,β -unsaturated ketones, β -chloro ketones, and saturated and unsaturated keto acids of normal and branched structure. This reaction was proposed in papers by Kondakov [1], Krapivin [2], Gustavson [3], and others. Kondakov studied the reaction of various alkenes (isobutene, 2-methyl-2-butene, and 2,3-dimethyl-2-butene) with acetic anhydride and with acetyl chloride in presence of zinc chloride, and he regarded it as an addition reaction. Krapivin studied the same reaction, but in presence of aluminum chloride, and he regarded it as a substitution reaction. We regard Kondakov's view on the mechanism of this reaction as the more correct, because we, and also other investigators, succeeded in isolating the primary reaction products, β -halo ketones. Somewhat later Blanc [4] applied Kondakov's reaction to unsaturated cyclic hydrocarbons. With the object of preparing α,β -unsaturated ketones, this reaction was studied by Scholler and Zöller [5], Colonge and Mostafavi [6], Stevens [7], Byrns and Doumani [8], Petrov and Kaplan [9] and others.

However, there is no discussion in the literature of the question of the relation of reactivity to structure for alkenes, acid anhydrides, and acid chlorides, and there is no information on the direction in which mixed anhydrides add to alkenes. Depending on their structures different alkenes, reacting with a given anhydride or acid chloride, form α,β -unsaturated ketones in different yields. Table 1 gives the yields of unsaturated ketones obtained by us in the reactions of acetic anhydride with alkenes of various structures in presence of zinc chloride.

It will be seen from Table 1 that the reactivity of alkenes depends on the number of alkyl groups attached at the double bond. Of the alkenes listed the most reactive is 2,3-dimethyl-2-butene, which, being a tetra-substituted ethylene, reacted most vigorously with acetic anhydride and gave 3,3,4-trimethyl-4-penten-2-one in 69% yield. The enhanced reactivity of 2,3-dimethyl-2-butene (tetramethylethylene) is to be explained by the influence of the methyl groups, which increase the electron density of the double bond of the alkene, facilitating the addition of the anhydride or acid chloride to the alkene (as compared to unsubstituted ethylene). 1,1-Dienopentylethylene [4,4-dimethyl-2-neopentyl-1-pentene] (the α -form of triisobutylene) reacts with acetic anhydride in presence of zinc chloride with formation of 6,6-dimethyl-4-neopentyl-3-hepten-2-one in 30% yield, whereas the monosubstituted ethylene 1-hexene, reacting with the same anhydride under the same conditions, give 4-octen-2-one in only 2.3% yield. The yield of the final reaction products in the acylation of olefins also depends substantially on the structure of the acid anhydride or chloride.

For the acylation we took acetic, butyric, isobutyric, and pivalic anhydrides and acetyl, butyryl, isobutyryl, hexanoyl, and octanoyl chlorides. Table 2 gives the yields (%) of unsaturated ketones obtained in the reaction of 2,3-dimethyl-2-butene with various acid anhydrides in presence of zinc chloride.

It will be seen that acid chlorides react with olefins in presence of metal halides somewhat more actively than the corresponding anhydrides with formation of β -chloro ketones, which are then converted into unsaturated ketones. With rise in molecular weight of the anhydride or acid chloride its reactivity falls. Increase in the branching of the acid also reduces the reactivity of its anhydride appreciably. When isobutyric anhydride is used the yield of ketones is only about one-third of that obtained in reaction with butyric anhydride, and pivalic anhydride does not react at all (steric hindrance).

TABLE 1

Original compounds acetic anhydride + the alkene:	Yield of unsaturated ketone (%)
$\text{CH}_2=\text{CH}_2$	Did not react
$\text{CH}_3-\text{CH}=\text{CH}-\text{CH}_3$	7,0
$\text{CH}_3-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2-\text{CH}_3$	2,3
$\text{CH}_3-\text{CH}=\text{C}-\text{CH}_3$	31,0
$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3-\text{C}=\text{C}-\text{CH}_3 \\ \quad \\ \text{CH}_3 \quad \text{CH}_3 \end{array}$	69,0
$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3-\text{C}-\text{CH}_2-\text{C}=\text{CH}_2 \\ \quad \\ \text{CH}_3 \quad \text{CH}_3 \end{array}$ $\left. \begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3-\text{C}-\text{CH}-\text{C}-\text{CH}_3 \\ \quad \\ \text{CH}_3 \quad \text{CH}_3 \end{array} \right\} \text{isomers}$	60,0
$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3-\text{C}-\text{CH}_2-\text{C}-\text{CH}_2-\text{C}-\text{CH}_3 \\ \quad \quad \\ \text{CH}_3 \quad \text{CH}_3 \quad \text{CH}_3 \end{array}$	30,0

As the anhydrides of higher acids, beginning from butyric and isobutyric anhydrides, are less reactive than acetic anhydride, it was of interest to determine the reactivities of mixed anhydrides in reactions with alkenes and find out which of the two acid residues of the mixed anhydride would react with the alkene, that of the higher or that of the lower acid. Mixed anhydrides were prepared and their reactions with ammonia, aniline, phenylhydrazine, and hydrazine hydrate were studied by Autenricht [10], and their stabilities were studied by Rousset [11] and Behal [12]. Gold and Jefferson [13] studied the hydrolysis and decomposition of acetic-formic mixed anhydride. Wieland and Stimming [14] studied the relative acylating powers of the acid residues in the mixed anhydrides of carboxylic acids for the case of reaction with hydroxylamine. To determine the reactivities of mixed anhydrides in their reactions with alkenes we studied the reaction of acetic-butyric mixed anhydride with 2,3-dimethyl-2-butene in presence of zinc chloride. The main product isolated was 2,3,3-trimethyl-2-hepten-4-one.* We synthesized the same ketone from butyric anhydride and 2,3-dimethyl-2-butene in presence of zinc chloride.

TABLE 2

Original compounds 2,3-Dimethyl-2-butene + the acid derivative	Yield of unsaturated ketone (%)
Acetic anhydride	69.0
Butyric anhydride	21.0
Isobutyric anhydride	6.3
Pivalic anhydride	Did not react
Isobutyryl chloride	9.3

TABLE 3

Original compounds Acid chloride of monoethyl adipate + alkene:	Yield of ethyl ester (%)
$\text{CH}_2=\text{CH}_2$	No reaction
$\text{CH}_3-\text{CH}=\text{CH}_2$	67.0
$\text{CH}_3-\text{CH}_2-\text{CH}=\text{CH}_2$	60.0
$\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}=\text{CH}_2$	44.0
$\begin{array}{c} \text{CH}_3-\text{C}=\text{C}-\text{CH}_3 \\ \quad \\ \text{CH}_2 \quad \text{CH}_2 \end{array}$	82.4

A mixture melting point test of the semicarbazone of the ketone obtained from acetic-butyric mixed anhydride and that of the ketone from butyric anhydride showed no depression. Hence, in the reaction of the mixed anhydride with the alkene in presence of zinc chloride it is mainly the acyl (cationoid) group of the higher acid which reacts with formation of the keto group, and the acid (anionoid) residue of the lower acid forms the ester grouping of the keto ester, which decomposes with liberation of the lower acid. Hence, no preliminary dis-

*In the Experimental Part the product is stated to be 2,3,3-trimethyl-1-hepten-4-one. — Translator.

proportionation of the mixed anhydride with formation of two simple (symmetrical) anhydrides occurs; otherwise, the main product would be an unsaturated ketone formed from the more reactive acetic anhydride.

The reactivities of the acid chlorides of dibasic acids and of their monoethyl esters also depend on the degree of branching of the acids. The acid chlorides of dimethyl- and diethyl-malonic acids and of the monoethyl esters of these acids are extremely inert and do not react with alkenes in presence of ZnCl_2 or SnCl_4 at $0-80^\circ$. Such inertness in the acid chlorides of branched acids is to be explained by steric hindrance due to their structures.

Table 3 shows that, as in the reactions with anhydrides and acid chlorides of monocarboxylic acids, the most reactive of the alkenes tried was 2,3-dimethyl-2-butene, which formed ethyl 8-chloro-7,8,8-trimethyl-6-oxononanoate in 82.4% yield. Comparing the yields of α,β -unsaturated ketones obtained from 2,3-dimethyl-2-butene and monocarboxylic anhydrides or acid chlorides (Table 2) with that of the ethyl ester of the chloro keto acid (Table 3) from the same alkene and the acid chloride of monoethyl adipate, we see that the latter is the most reactive acylating agent.

EXPERIMENTAL

The acylation of olefins with anhydrides and acid chlorides was carried out under the conditions described previously [15].

3-Methyl-3-penten-2-one was prepared from 2-butene and acetic anhydride in presence of zinc chloride at 20° for 12 hours. For the synthesis we took 420 g of acetic anhydride (b.p. $137-138^\circ$), 224 g of 2-butene, and 136 g of ZnCl_2 . Unchanged 2-butene (130 g) was condensed at -73° . The main reaction product was decomposed with water in the cold. The upper layer was separated, washed with a little water, neutralized with saturated sodium carbonate solution, and washed with water. As much resinification occurred, the reaction product was extracted with ether, which was then distilled off. Fractionation gave 25 g (7%) of ketone; b.p. $138-140^\circ$; d_4^{20} 0.8440; n_D^{20} 1.4475; found MR 29.95; calculated MR 29.45.

The semicarbazone had m.p. 177° . Found: N 26.49%. $\text{C}_7\text{H}_{13}\text{ON}_3$. Calculated: N 27.00%.

4-Octen-2-one was prepared by the reaction of 1-hexene with acetic anhydride in presence of zinc chloride. The reaction was carried out at 40° with stirring for 18 hours. The yield of ketone was 2.3%; d_4^{20} 0.8740; n_D^{20} 1.4439; found MR 38.68; calculated MR 39.64.

3,3,4-Trimethyl-4-penten-2-one was synthesized under the conditions described by Meshcheryakov and Petrova [16].

2,3,3-Trimethyl-1-hepten-4-one* was prepared from 2,3-dimethyl-2-butene and butyric anhydride in presence of zinc chloride. For the synthesis we took 70 g of 2,3-dimethyl-2-butene, 76 g of butyric anhydride, and 30 g of zinc chloride. The experiment was carried out at $40-50^\circ$. Fractionation gave a ketone in 20.6% yield; b.p. $180-183^\circ$; d_4^{20} 0.8631; n_D^{20} 1.4365; found MR 46.62; calculated MR 47.92. The discrepancy in the MR values indicates the presence of 2,3-dimethyl-2-butene dimer impurity. Molecular weight of the ketone: found M 153.3; $\text{C}_{10}\text{H}_{18}\text{O}$. Calculated M 154.0 for the monomer. The semicarbazone had m.p. $138-139^\circ$. Found: N 19.13%. $\text{C}_{11}\text{H}_{21}\text{N}_3\text{O}$. Calculated: N 19.52%.

2,4,4,5-Tetramethyl-5-hexen-3-one was prepared from 2,3-dimethyl-2-butene and isobutyryl chloride (b.p. $92-94^\circ$) in presence of zinc chloride in 7.7% yield, and in presence of stannic chloride in 9.3% yield. 2,4,4,5-Tetramethyl-5-hexen-3-one has b.p. $165-170^\circ$; d_4^{20} 0.8572; n_D^{20} 1.4385; found MR 46.77; calculated MR 46.74. Found: C 77.13; H 11.85%. $\text{C}_{10}\text{H}_{18}\text{O}$. Calculated: C 77.90; H 11.69%.

The semicarbazone has m.p. $188-189^\circ$. Found: N 18.83%. $\text{C}_{11}\text{H}_{21}\text{N}_3\text{O}$. Calculated: N 19.52%.

A Mixture of 4,6,6-trimethyl-3-hepten-2-one and 3-isopropyl-4,4-dimethyl-3-penten-2-one was synthesized from Butlerov's diisobutylene (80% of 2,4,4-trimethyl-1-pentene and 20% of 2,4,4-trimethyl-2-pentene) and acetic anhydride in presence of zinc chloride [8]. The mixture of ketones obtained had the following properties: b.p. $65-68^\circ$ (2 mm); d_4^{20} 0.8419; n_D^{20} 1.4467; found MR 48.08; calculated MR 47.93. Found: C 77.31; H 11.63%. $\text{C}_{10}\text{H}_{18}\text{O}$. Calculated: C 77.92; H 11.70%.

* See footnote, p. 89.

The 2,4-dinitrophenylhydrazone had m.p. 159–160°. Found: N 16.67%. $C_{16}H_{22}O_4N_4$. Calculated: N 16.76%.

The syntheses of 6,6-dimethyl-4-neopentyl-3-hepten-2-one, 2,7,7-trimethyl-5-neopentyl-4-octen-3-one, and 2,5,7,7-tetramethyl-4-octen-3-one have been described previously [15].

Addition of acetic-butyric mixed anhydride to 2,3-dimethyl-2-butene. The mixed anhydride of acetic and butyric acids was prepared from butyric acid and ketene in 56% yield; b.p. 165–175°. For the reaction we took 33.2 g of 2,3-dimethyl-2-butene, 51.5 g of acetic-butyric mixed anhydride, and 10.0 g of zinc chloride. Reaction was at 40–50° with stirring for 12 hours. The reaction product was treated as in the above-described experiments. The amount of 2,3-dimethyl-2-butene that reacted was 13.2 g. Two fractionations through a column of 18-plate efficiency gave a main reaction product of b.p. 180–182°; yield 12.2 g (81% on the 2,3-dimethyl-2-butene that reacted); d_4^{20} 0.8280; n_D^{20} 1.4265; found MR 47.45; calculated MR 47.92.

The semicarbazone had m.p. 139–140°, undepressed by admixture of the semicarbazone of the ketone prepared from butyric anhydride and 2,3-dimethyl-2-butene (m.p. of mixture 138.5–139.5°). Found: N 19.18%; $C_{11}H_{21}N_3O$. Calculated N 19.52%. Molecular weight: found M 152.4. $C_{10}H_{18}O$. Calculated M 154.0.

Ethyl 8-chloro-6-oxononanoate was prepared from propene and the acid chloride of monoethyl adipate in presence of zinc chloride. The experiment was carried out in an autoclave at 20–25° under 7 atm. We took 170 g of the acid chloride of monoethyl adipate, 28 liters of propene, and 17.0 g of zinc chloride. The yield of the ester was 131 g (66.8%); b.p. 118–122° (4 mm) (during fractionation decomposition occurred with liberation of HCl); d_4^{20} 1.0070; n_D^{20} 1.4350; found MR 60.54; calculated MR 59.53.

Ethyl 8-chloro-6-oxodecanoate was synthesized from 1-butene and the acid chloride of monoethyl adipate in presence of zinc chloride. The acid chloride of monoethyl adipate was prepared from monoethyl adipate and phosphorus trichloride; it had the following properties: b.p. 155–158° (60 mm); d_4^{20} 1.0890; n_D^{20} 1.4399; found MR 46.38; calculated MR 46.81. The literature [17] gives b.p. 128° (17 mm). The ester was synthesized in a long-necked metal flask, which was first cooled. It was charged with the reactants: 225 g of the acid chloride of monoethyl adipate, 144 g of liquid 1-butene, and 16 g of zinc chloride. The reaction mixture was agitated vigorously in a shaker: 2 hours at 0°, and then 6 hours at 20°. Unchanged 1-butene was condensed in a trap, which was cooled with a mixture of solid carbon dioxide and acetone. The amount of 1-butene that reacted was 90 g. The reaction product was washed with water, with 5% sodium carbonate solution, and again with water, dried over calcium chloride, and vacuum-fractionated; b.p. 145–150° (6 mm) (partial decomposition occurred in the fractionation with elimination of HCl). Yield of the ester 60%; d_4^{20} 1.0098; n_D^{20} 1.4363; found MR 64.09; calculated MR 64.14.

Ethyl 8-chloro-6-oxododecanoate was prepared from 1-hexene and the acid chloride of monoethyl adipate. The amounts taken for reaction were 45 g of 1-hexene, 67 g of the acid chloride of monoethyl adipate, and 6 g of zinc chloride. The reaction was carried out in a 500-ml round-bottomed flask fitted with mercury-sealed stirrer and spherical condenser. Reaction was for 18 hours at 20°. The reaction product was decomposed with water and treated as in the above-described synthesis. Fractionation gave 37 g (44%) of ethyl 8-chloro-6-oxododecanoate; b.p. 160–168° (30 mm); d_4^{20} 1.0023; n_D^{20} 1.4348; found MR 72.23; calculated MR 73.38. The discrepancy in the values of molecular refraction is to be explained by the occurrence of fairly considerable decomposition of the reaction product during fractionation, with liberation of HCl.

Ethyl 8-Chloro-7,7,8-trimethyl-6-oxononanoate was prepared from 2,3-dimethyl-2-butene and the acid chloride of monoethyl adipate. The experiment was carried out under the conditions described above. For the synthesis we took 137 g of the acid chloride of monoethyl adipate, 60 g of 2,3-dimethyl-2-butene, and 6 g of zinc chloride. The reaction product was decomposed with water in the cold and treated in the usual way. Fractionation gave 160 g (82.4%) of the ester; b.p. 152–155° (8 mm); n_D^{20} 1.4529; d_4^{20} 0.9822; found MR 67.03; calculated MR 69.52. During distillation decomposition occurred, with elimination of HCl.

SUMMARY

1. The reactivities of alkenes in reactions with monocarboxylic anhydrides and acid chlorides, and acid chlorides of monoethyl esters of dicarboxylic acids in presence of metal halides depend substantially on the structures of the original alkenes. From a comparison of the reactions of 1-hexene and 2,3-dimethyl-2-butene with acetic anhydride and the acid chloride of monoethyl adipate it was shown that the branched alkene had the greater reactivity.

2. In their reactions with alkenes the reactivities of monocarboxylic anhydrides and acid chlorides and dicarboxylic acid chlorides also depend on the structures of the latter. The behavior of 2,3-dimethyl-2-butene with pivalic anhydride and the acid chlorides of the monoethyl esters of dimethyl- and diethyl-malonic acids indicates the inertness of the latter, which is determined by their highly branched structures.

3. In the reaction of a mixed anhydride with an alkene in presence of zinc chloride, the acyl group of the higher acid adds at the double bond with formation of the keto group of the product.

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* Original Russian pagination. See C. B. Translation.

STERIC HINDRANCE AND THE CONFORMATION OF MOLECULES

COMMUNICATION 1. STERIC HINDRANCE IN THE MOLECULES OF POLYHALOBENZENES AND THEIR DERIVATIVES

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Translated from *Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk* 1960, No. 1

pp. 104-110, January 1960

Original article submitted June 14, 1958

The classical problem of steric hindrance has recently acquired highly topical significance in connection with the development of so-called conformational analysis, i.e., with the realization that the mutual effects of atoms in a molecule are not confined to interaction through covalent bonds and that the form (configuration, conformation) of a molecule, and in some cases also its reactivity, depends also on interactions between atoms not bound together by valences. If the distances between these atoms are less than the sums of their van der Waals (intermolecular) radii, repulsion forces begin to predominate over attractive forces and the molecule will be sterically strained, i.e. possess increased energy. Naturally, this steric hindrance might be removed, i.e. the distances between nonvalently bound atoms might be increased to the normal value by change in other geometric parameters of the molecule, i.e. its bond lengths and valence angles. However, theoretical calculations and numerous experimental facts [1, 2] show that the force constants for the stretching of bonds are much greater than those for the distortion of valence angles, the energy of which is comparable to that of van der Waals interaction. Hence, the only possibility for the removal of steric hindrance must be the distortion of valence angles or rotation around single bonds, which can result in partial breakdown of the conjugation between parts of the molecule united by these bonds (e.g. in biphenyl and its derivatives) or destruction of the coplanarity of the system (e.g. in dibenzo [c, g] phenanthrene). Hence, in these cases there is a definite interaction between van der Waals repulsion and the chemical forces striving to maintain the coplanarity of the molecule.

Hence, the once indefinite term "steric hindrance" has now acquired a definite meaning: repulsion between nonvalently bound atoms resulting in an increase in the energy of the molecule and in change in its "normal" conformation (which, in absence of this hindrance, would be the most favorable one), i.e., a repulsion that leads to the distortion of valence angles and rotations around single bonds and disturbance of coplanarity which are unfavorable to conjugation. Despite the great progress made in the understanding of the nature of steric hindrance, we are still a long way from its quantitative description, i.e. the establishment of the relation between van der Waals compression and the change in angular parameters. The main cause of this lies both in the absence of a quantitative expression for the potential of van der Waals interaction and in the arbitrary sense of the deformation constants of valence angles. Theoretical calculations [2] of this potential still require such serious assumptions and simplifications that their significance is extremely doubtful. It is not by chance, therefore, that in most cases the part played by steric hindrance is estimated a posteriori, i.e. it is made to account for unusual behavior of molecules in reactions which cannot be explained by other factors, and the peculiarities of reactivity (stereospecificity in the wide meaning of the word) are not predicted on the basis of concrete geometric parameters of the molecules and, in particular, of the steric hindrance present.

The complicated character of a satisfactory theoretical calculation of the part played by steric hindrance makes it most expedient (with the proviso "at the present time and for practical purposes") to adopt a semi-empirical approach to the problem, i.e. the establishment of the relation between van der Waals compression and the distortion of valence angles by the study of the geometry of a large number of sterically strained molecules. The most direct method of establishing this relation will be the study of the statistical geometry of molecules, because conclusions based on reactivity will of necessity be ambiguous because of lack of knowledge of the geometry of the transition state. In this way a direct link is established between conformational analysis and organic crystal chemistry, which is the most powerful instrument for the investigation of "frozen" molecules.

The fundamental ideas of organic crystal chemistry, which were formulated and developed on the basis of much experimental material by Kitaigorodskii in his monograph [1] and in many later articles, will undoubtedly find a broad field of application in the treatment of problems of the geometry of molecules and, in particular, conformational analysis.

The study of statistical deformations in sterically strained or, as they are sometimes called, "overcrowded" molecules is of interest also in that these deformations can probably serve as a model for the dynamic distortions resulting from the approach of a reagent molecule to a normal (unstrained) molecule during a reaction. These distortions are not, of course, amenable to direct observation; nevertheless, the character of the deformation of a molecule due to the entry of a reagent molecule, particularly if not carrying a charge, into the van der Waals repulsion region and also the structure of the active complex formed by the "merging" of the two components may be readily understood on analogy with "overcrowded" structures.

In many respects, the greatest interest is presented by the study of sterically strained aromatic systems, which may be conveniently divided [3] into four groups*: 1) substituted benzenes, e.g. o-dichlorobenzene (I) and durene [1,2,4,5-tetramethylbenzene] (II); 2) polycyclic systems, e.g. dibenzo [c,g] phenanthrene (III) and dibenzo [a, c] triphenylene (IV); 3) tetraphenylethylenes with bridges in all the 2-positions of the phenyl groups, e.g. $\Delta^{9,9}$ -bifluorene (V) $\Delta^{10,10}$ -bianthrone (VI); 4) molecules with an "excess" of phenyl or phenylene groups, e.g. 1,4,5,8-tetraphenylnaphthalene (VII) and the double p- and m-xylene molecules (VIII) and IX).

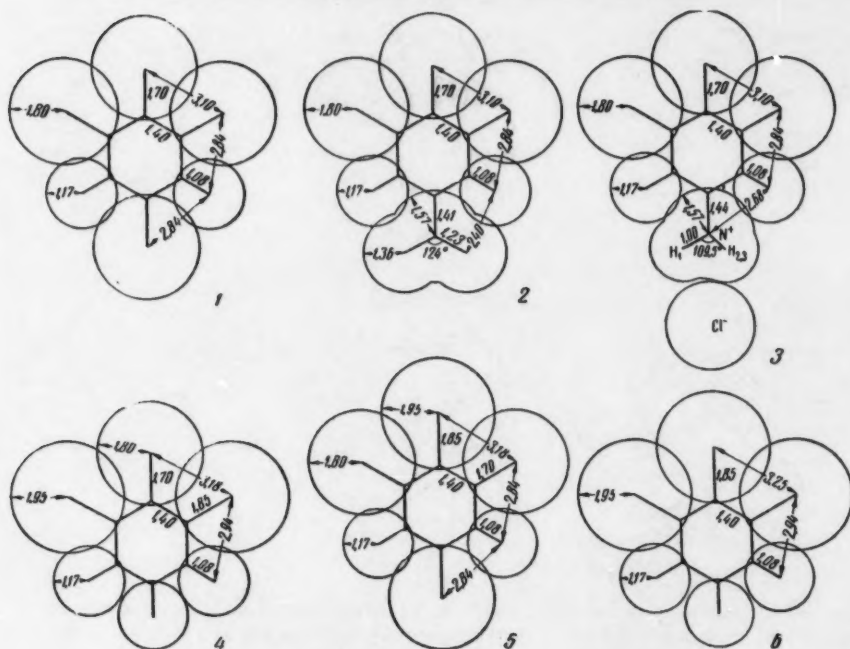
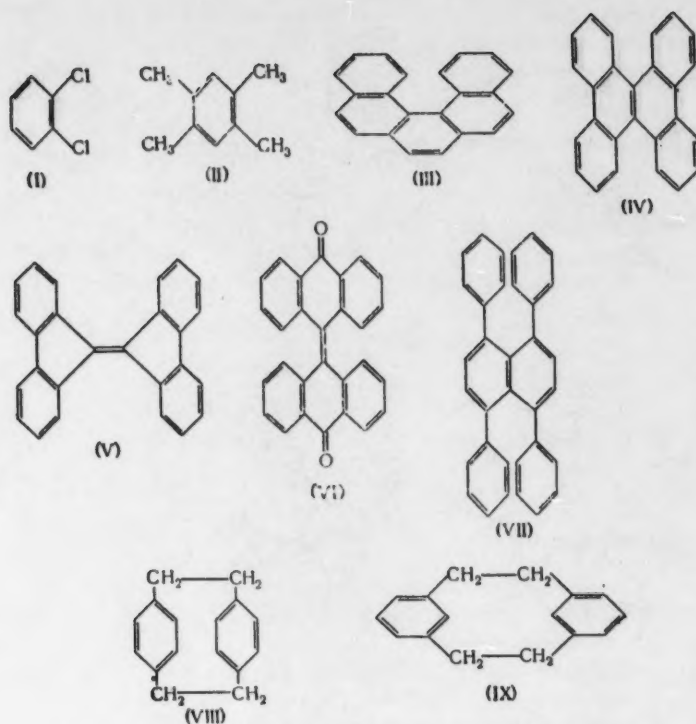
Unfortunately, none of these groups has yet been investigated in any detail.

Successful attempts to analyze the conformations of "flexible" molecules based on a simple estimation of steric hindrance as the sum of the reductions in distance between nonvalently linked atoms may be found in papers on the structures of tetraiodoethylene [4], iodoform [5], diphenyliodonium halides [6], tetraphenylphosphonium iodide [7] and other compounds; these investigations were carried out in the X-ray Structure Analysis Laboratory of our Institute. However, these same investigations revealed the necessity of making a systematic study of a large series of molecules which are simple in the geometric sense, i.e. molecules whose steric hindrance is described by the minimum number of parameters. In this respect polysubstituted benzenes are very attractive, because their molecules are based on the relatively rigid benzene ring so that steric hindrance should amount mainly to interaction between ortho substituents with an accompanying distortion of valence angles external with respect to the ring. Among these the most suitable objects of study will be the polyhalobenzenes, for the halogen atoms can be readily and accurately located by x-rays; reliable values of intermolecular radii are known for them, and the synthesis of these compounds is fairly simple.

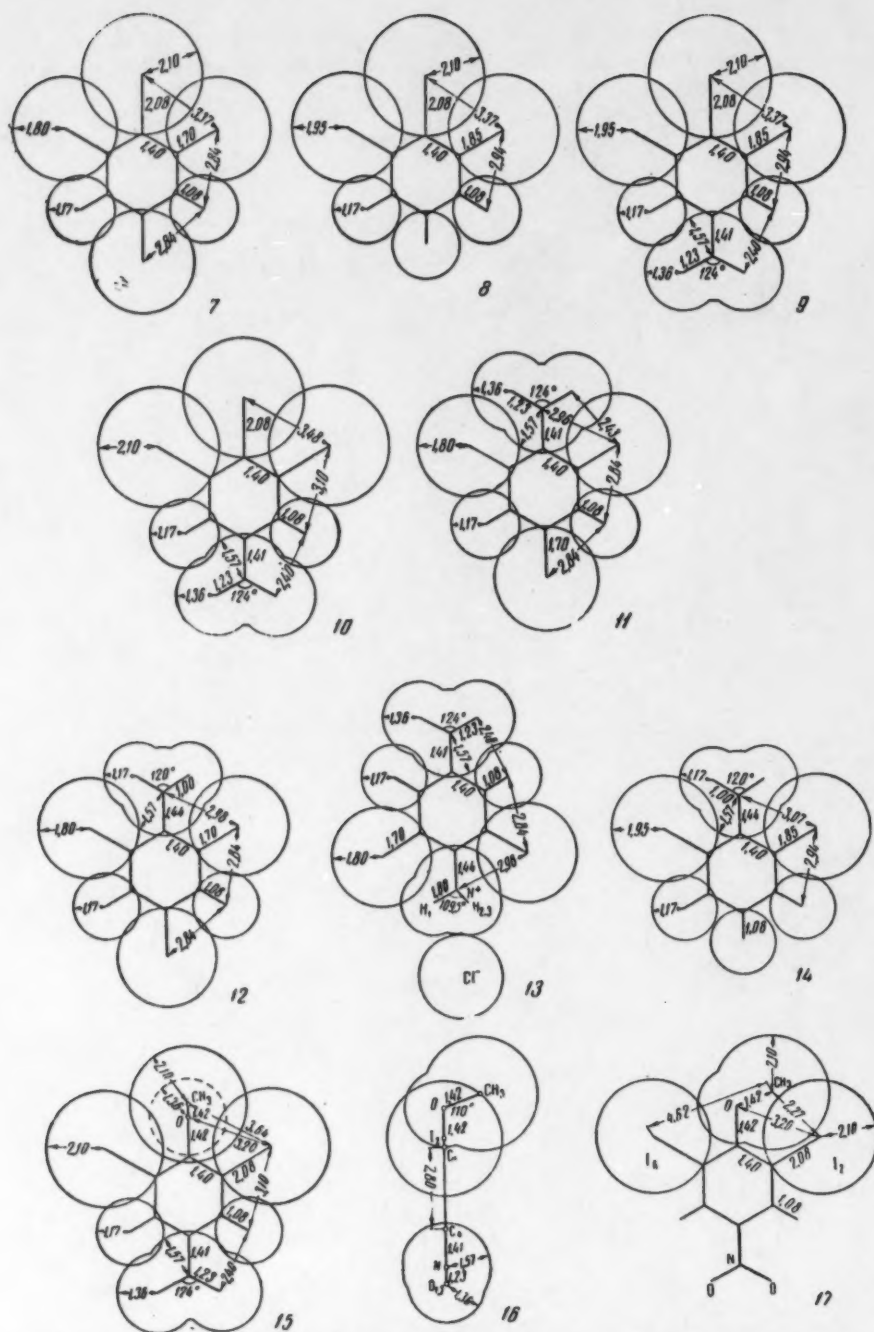
We carried out a preliminary x-ray structure investigation of fifteen compounds of this type. Below we give a table and Figures 1-17 illustrating steric strain in their molecules. In the calculation of steric hindrance, i.e. the distances between nonvalently linked atoms, it was assumed that the molecules had their ideal configurations, i.e. were flat (coplanar), had normal valence angles (120°), and the usual bond lengths: C-C = 1.40; C-H = 1.08; C-Cl = 1.70; C-Br = 1.85; C-I = 2.08; C-N (nitro group) = 1.41; C-N (amino group) = 1.44; C-O = 1.42; N-O = 1.23; N-H = 1.00 Å. Standard values were assumed for intermolecular radii: $R_C = 1.80$; $R_H = 1.17$; $R_O = 1.36$; $R_N = 1.57$; $R_{Cl} = 1.80$; $R_{Br} = 1.95$; $R_I = 2.10$ Å. The methyl group was regarded as a sphere of radius 2.10 Å. The nitro group was considered to be coplanar with the benzene ring, and the ammonium grouping as tetrahedral with valence angles of 109.5° . The calculation of the steric hindrance in the molecule of 2,6-diiodo-4-nitroanisole was carried out for two configurations: with the methoxy group in the plane of the benzene ring and with it perpendicular to the benzene ring (in Figures 15-17 this configuration is represented in two projections).

In the table, D denotes the distance between the centers of atoms not linked through a valence, D' denotes the sum of the corresponding intermolecular radii, and $\Delta D = D' - D$, the difference between these quantities, which is a measure of the steric hindrance between the given pair of atoms. At the present stage of development of the problem of steric hindrance, as a measure of the total steric strain of the molecule we may take the sum of the contractions, i.e. $\Sigma \Delta D$, taken over all pairs of atoms; the values of this are also given in the table. It is obvious that in the future more rigorously definable parameters will be worked out for steric strain.

* o-Derivatives of biphenyl can with equal right be assigned to the first or the fourth group.



Figures 1 - 6. Geometry of ideal molecules of polyhalobenzenes and their derivatives; 1) 1,2,3,5-tetrachlorobenzene; 2) 1,2,3-trichloro-5-nitrobenzene; 3) 3,4,5-trichloroaniline hydrochloride; 4) 1,3-dibromo-2-chlorobenzene; 5) 2-bromo-1,3,5-trichlorobenzene; 6) 1,2,3-tribromobenzene.



Figures 7-17. Geometry of ideal molecules of polyhalobenzenes and their derivatives: 7) 1,3,5-trichloro-2-iodobenzene; 8) 1,3-dibromo-2-iodobenzene; 9) 1,3-dibromo-2-iodo-5-nitrobenzene; 10) 1,2,3-triiodo-5-nitrobenzene; 11) 1,3,5-trichloro-2-nitrobenzene; 12) 2,4,6-trichloroaniline; 13) 2,6-dichloro-4-nitroaniline hydrochloride; 14) 2,6-dibromoaniline; 15-17) 2,6-diiodo-4-nitroanisole.

In most of the molecules the steric hindrance is very considerable. It is known that the relation between the contraction ΔD in the distance between atoms not linked by a valence and the corresponding distortion of the valence angle $\Delta\varphi$ is approximately as follows [1]:

$\Delta D(\text{\AA})$	0,3	0,5	0,8
$\Delta\varphi(\text{degrees})$	5	10	25

TABLE

Steric Hindrance in Molecules of Polyhalobenzenes and their Derivatives

Compound	D (A)	D' (A)	$\Delta D(\text{\AA})$	$\Sigma\Delta D(\text{\AA})$
1,2,3,5-Tetrachlorobenzene (see Fig. 1)	Cl—Cl=3,10 Cl—H=2,84	Cl—Cl=3,60 Cl—H=2,95	0,50 0,11	1,44
1,2,3-Trichloro-5-nitrobenzene (see Fig. 2)	Cl—Cl=3,10 Cl—H=2,84 H—O=2,40	Cl—Cl=3,60 Cl—H=2,95 H—O=2,53	0,50 0,11 0,13	1,48
3,4,5-Trichloroaniline hydrochloride (see Fig. 3)	Cl—Cl=3,10 Cl—H=2,84 H—N=2,68	Cl—Cl=3,60 Cl—H=2,95 H—N=2,74	0,50 0,11 0,06	1,34
1,3-Dibromo-2-chlorobenzene (see Fig. 4)	Cl—Br=3,18 Br—H=2,94	Cl—Br=3,75 Br—H=3,12	0,57 0,18	1,50
2-Bromo-1,3,5-trichlorobenzene (see Fig. 5)	Br—Cl=3,18 Cl—H=2,84	Br—Cl=3,75 Cl—H=2,95	0,57 0,11	1,58
1,2,3-Tribromobenzene (see Fig. 6)	Br—Br=3,25 Br—H=2,94	Br—Br=3,90 Br—H=3,12	0,65 0,18	1,66
1,3,5-Trichloro-2-iodobenzene (see Fig. 7)	I—Cl=3,30 Cl—H=2,84	I—Cl=3,90 Cl—H=2,95	0,60 0,11	1,64
1,3-Dibromo-2-iodobenzene (see Fig. 8)	I—Br=3,37 Br—H=2,94	I—Br=4,05 Br—H=3,12	0,68 0,18	1,72
1,3-Dibromo-2-iodo-5-nitrobenzene (see Fig. 9)	I—Br=3,37 Br—H=2,94 H—O=2,40	I—Br=4,05 Br—H=3,12 H—O=2,53	0,68 0,18 0,13	1,98
1,2,3-Trifluoro-5-nitrobenzene (see Fig. 10)	I—I=3,48 I—H=3,40 H—O=2,40	I—I=4,20 I—H=3,27 H—O=2,53	0,72 0,17 0,13	2,04
1,3,5-Trichloro-2-nitrobenzene (see Fig. 11)	Cl—N=2,96 Cl—O=2,43 Cl—H=2,84	Cl—N=3,37 Cl—O=3,16 Cl—H=2,95	0,41 0,73 0,11	2,72
2,4,6-Trichloroaniline (see Fig. 12)	Cl—N=2,98 Cl—H=2,84	Cl—N=3,37 Cl—H=2,95	0,39 0,11	1,44
2,6-Dichloro-4-nitroaniline hydrochloride (see Fig. 13)	H—O=2,40 Cl—H=2,84 Cl—N=2,98	H—O=2,53 Cl—H=2,95 Cl—N=3,37	0,13 0,11 0,39	1,37
2,6-Dibromoaniline (see Fig. 14)	Br—N=3,07 Br—H=2,94	Br—N=3,52 Br—H=3,12	0,45 0,18	1,62
2,6-Difluoro-4-nitroanisole; a) methoxy group perpendicular to the nucleus (see Fig. 15 and 16); b) methoxy group in plane of nucleus (see Fig. 17)	I—O(CH ₃)=3,20 I—CH ₃ =3,64 I—H=3,40 H—O(NO ₂)=2,40 I—O(CH ₃)=3,20 I ₂ —CH ₃ =2,27 I ₆ —CH ₃ =4,62 I—H=3,40 H—O(NO ₂)=2,40	I—O=3,46 I—CH ₃ =4,20 I—H=3,27 H—O=2,53 I—O=3,46 I—CH ₃ =4,20 I—CH ₃ =4,20 I—H=3,27 H—O=2,53	0,26 0,56 0,17 0,13 0,26 1,93 — 0,17 0,13	2,24 — 3,05

Hence, appreciable distortion of valence angles must be expected in many of the molecules under consideration. The greatest steric hindrance is found in the molecules of 1,3,5-trichloro-2-nitrobenzene and 2,6-difluoro-4-nitroanisole. In the case of 1,3,5-trichloro-2-nitrobenzene the nitro group must undoubtedly be turned in a direction perpendicular to the nucleus. However, even then the residual steric hindrance is very great, i.e. distortion of valence angles must occur. We have shown experimentally that in the molecule of 2-bromo-1,3,5-trichloro-benzene, in which the sum of the contractions is 1.58 Å, there is a considerable distortion of valence angles. Hence, measurable deformations must be found in all molecules for which $\Sigma\Delta D \approx 1.6$ Å; this condition is satisfied by nine of the fifteen compounds investigated.

SUMMARY

1. Conformational analysis is based on an estimation of the steric hindrance in molecules, which still has a semiempirical character because of the absence of a satisfactory method for the calculation of the van der Waals potential and the conditional nature of the deformation constants of valence angles.

2. Quantitative conformational analysis must be based on a study of the relation of deformations of valence angles and of breakdown of conjugation to the contractions in the distances between atoms of the molecule that are not linked through valences.

3. Analysis of steric hindrance in polyhalobenzenes and their derivatives indicates the presence of substantial steric strain, which must be accompanied by a considerable departure of the form of the molecule from the ideal form.

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CATALYTIC POLYMERIZATION OF OLEFINS

COMMUNICATION 3. ACTIVITY OF A NICKELOUS OXIDE - SILICA GEL CATALYST IN THE POLYMERIZATION OF ETHYLENE

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Translated from *Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk* 1960,

No. 1, pp. 111-114, January 1960

Original article submitted May 4, 1958

From a review of investigations [1] on the polymerization of ethylene in presence of heterogeneous catalysts it is seen that neither silica gel [2] nor nickel (or nickelous oxide) [3] is a catalyst for the polymerization of ethylene. There are contradictory data in the literature regarding nickelous oxide - silica gel catalysts [4]. It has been stated [5] that the activity of an $\text{NiO}-\text{SiO}_2$ catalyst in this reaction is associated with its dehydration by heat in a vacuum, though there is reason to suppose that in this case the carrier was not SiO_2 , but a form of Japanese clay, which evidently contained not only SiO_2 , but also Al_2O_3 .

Our object in the present investigation was the study of the activities, in the polymerization of ethylene, of catalysts in which nickelous oxide is deposited on silica gels of various origins. We used both precipitated and impregnation catalysts, for the preparation of which we used solutions of nickel nitrate, sulfate, and formate.

EXPERIMENTAL

The experiments on the polymerization of ethylene were carried out in a flow system in a reactor consisting of a glass tube, 10 mm in diameter. Ethylene was prepared by the dehydration of ethanol over commercial "chemically pure" alumina. The original gas, which contained 96-99% of ethylene, was purified and dried and passed over the catalyst in the reaction tube, which was heated in a catalysis furnace fitted with an automatic thermoregulator. The temperature in the furnace was constant within $\pm 1.5^\circ$. From the reaction tube the gas passed through three successive traps, of which the last two were cooled to -80° . The outgoing gas, and also the C_3-C_4 fraction distilled from the liquid condensate, was analyzed by the sulfuric acid method. The experiments, which each lasted five hours, were carried out at 300° , and the time of contact with the catalyst was 12-17 seconds.

Experiments with catalysts prepared from nickel nitrate and sulfate. Some of the catalysts studied were prepared by the impregnation of silica gel with a saturated solution of nickel sulfate or nitrate. We tested fifteen samples of silica gel, which were obtained commercially or were prepared by us by precipitation of sodium silicate solution with sulfuric or hydrochloric acid. In particular we tried ASM, ASK, ShSK, ShSM, MSM, and KSM silica gels. All these catalysts lost nickel salt when washed free from nitrate ions; they were decolorized and were quite inactive for the polymerization of ethylene after treatment in a stream of air at 300° .

Catalysts prepared analogously by precipitation with aqueous ammonia from dilute or saturated nickel nitrate solutions on the silica gels enumerated above, with subsequent washing free from nitrate ions and heating in a stream of air at 300° , were also inactive.

During the polymerization experiments these catalysts did not alter in color. Only KSK silica gel was found to be suitable for the preparation of catalysts from nickel nitrate both by the impregnation method (Catalysts 31, 33, and 34, Table 1) and by the precipitation method (Catalyst 32, Table 2).

Tables 1 and 2 show that $\text{NiO}-\text{KSK}$ silica gel catalysts give conversions of ethylene of 40-53% and yields of butene and liquid products of 22-32% and 7-11%, respectively, on the ethylene that reacts. However, these results refer to the first five hours of the work of the catalyst (to the first experiment). In the next five hours the activity falls by more than 50%. The low catalytic stability is due to the formation of a carbonaceous mass on the surface, which can be seen from the appearance of the spent catalyst. Catalysts prepared from KSK silica gel by the use of nickel sulfate solution by the impregnation or precipitation method were less active. The activities of the catalysts did not depend on whether they had been treated with air at 300° beforehand, but were the same

TABLE 1

Polymerization of Ethylene over an Impregnation Catalyst of NiO on KSK Silica Gel

Number		Contact	Yield of butene(%)		Yield of higher hydrocarbons(%)	
catalyst	expt.	period (sec)	on ethylene passed	on ethylene reacted	on ethylene passed	on ethylene reacted
33	1-2	12-12	22-7	55-43	8-2	20 -12
31	1-2	17-16	28-4.5	52-23	10-1	18.5-4.5
31	3-4	33-28	20-18	48-49	7-6	17 -16
34	1-2	32-32	32-16	64-57	11-4.5	22 -16
34	3	32	9	24	2	6.5

TABLE 2

Polymerization of Ethylene over a Precipitation Catalyst of NiO on KSK Silica Gel

Number		Contact	Yield of butene(%)		Yield of higher hydrocarbons(%)	
catalyst	expt.	period (sec)	on ethylene passed	on ethylene reacted	on ethylene passed	on ethylene reacted
32	1-2	15-14	31-13	64-60	7-3	14-13
32	3	16	8	66	1	8

when ethylene was passed over them immediately at this temperature; reduction of the catalysts with hydrogen at 300° for three hours reduced their activity somewhat. It is noteworthy that catalysts prepared by the same method, but on carriers from different samples of KSK silica gel differed very greatly in activity. This indicates that the composition or structure of the silica gel varies from sample to sample.

Experiments with catalysts prepared from nickel formate. Catalysts prepared by impregnation with boiling 1% or concentrated nickel formate solution using several samples of commercial silica gel [ShSK, ASK (Catalyst 42)], and also a sample which we prepared by precipitating sodium silicate solution with hydrochloric acid (Catalyst 79) and an aerogel prepared from this sample in an autoclave at 250° and 210 atm with treatment with alcohol [6], were not very active (Table 3) or were quite inactive after being heated at 300° in a stream of air or ethylene.

An analogous catalyst prepared from a sample of KSK silica gel had some activity, but other catalysts prepared in the same way from other samples of KSK silica gel had different activities; some of them were of extremely low activity, which was observed, as stated above, also with impregnation catalysts prepared with nickel nitrate on the same silica gel.

TABLE 3

Polymerization of Ethylene over Impregnation NiO-Silica Gel Catalysts

Number		Contact	Yield of butene (%)		Yield of higher hydrocarbons (%)	
catalyst	expt.	period (sec)	on ethylene passed	on ethylene reacted	on ethylene passed	on ethylene reacted
75	1	11	8.5	45.5	1.7	9
42	1-2	12-19	6.1-5.0	47.0-38.0	1.8-2.4	14.0-18.5

Over the most active of these catalysts, which was prepared from nickel formate and KSK silica gel (Catalyst 60, Table 4), with a contact period of 11 seconds ethylene reacted to the extent of 31.3% in the first five hours, and the yields of butene and liquid condensate were, respectively, 25.4% and 6.0% on the ethylene passed and 81.3% and 19.2% on the ethylene that reacted. However, in the next five hours the yields (on the ethylene passed) were reduced by almost one-half.

TABLE 4

Polymerization of Ethylene over an Impregnation Catalyst of NiO on KSK Silica Gel

Number		Contact	Yield of butene (%)		Yield of higher hydrocarbons (%)	
catalyst	expt.	period (sec)	on ethylene passed	on ethylene reacted	on ethylene passed	on ethylene reacted
60	1-2	11	25.4-12.6	81.3-70.5	6.0-1.6	19.2-9.2
60	3	11	11.7	83.0	1.6	11.6
58	1	12	0.0	0.0	0.0	0.0

Experiments with KSK silica gel. In absence of nickelous oxide, KSK silica gel was quite inactive in the polymerization of ethylene. When it was removed from the reaction tube it was found to have browned and even blackened portions. Our results show that an NiO catalyst deposited on various samples of silica gel is generally inactive in the polymerization of ethylene. The catalyst NiO - KSK silica gel is active, but is of low catalytic stability. KSK silica gel alone is not a catalyst for the polymerization of ethylene. It is noteworthy that NiO - KSK silica gel prepared from different samples of this silica gel varies in activity. This is probably to be explained by the presence of some unknown impurity in the silica gel, the amount of which is sometimes greater and sometimes less. We cannot exclude the possibility that the activity of KSK silica gel as a carrier for an NiO catalyst in the polymerization of ethylene is to be attributed to this impurity. Numerous examples can be cited in which silica gel that is catalytically inactive or of low activity becomes active, or even extremely active, after the adsorption of small amounts of alumina [7-9]. It may be supposed that, in the present case also, the activity is due to alumina impurity in KSK silica gel, so that the properties of an aluminum silicate are then ascribed to a silica gel. The investigation of this question is of great interest, and its solution should be approached by a study of the effect of additions of alumina on the properties of KSK silica gel as a carrier for an NiO catalyst for the polymerization of ethylene.

SUMMARY

1. Of fifteen different samples of silica gel, only one (KSK) was found to be suitable as a carrier for active nickel catalysts for the polymerization of ethylene.
2. KSK silica gel alone is not a catalyst for the polymerization of ethylene.
3. Catalysts of differing activities are obtained from different samples of KSK silica gel, which indicates that the composition or structure of this silica gel varies from sample to sample. It is suggested that the activities of the catalysts are associated with the presence of alumina impurity in the silica gel.

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CATALYTIC POLYMERIZATION OF OLEFINS

COMMUNICATION 4. POLYMERIZATION OF ETHYLENE OVER A NICKELOUS OXIDE - SILICA GEL CATALYST PROMOTED WITH ALUMINA

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Translated from *Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk* 1960,

No. 1, pp. 115-119, January 1960

Original article submitted May 21, 1958

It was previously shown [1] that nickelous oxide on silica gels of various origin did not act as a catalyst for the polymerization of ethylene. Only KSK silica gel was found to be suitable as a carrier; but when different samples of this were used, catalysts of different, usually extremely low, activities were obtained. This behavior was attributed to some alumina impurity, the amount of which appeared to vary.

The activating effect of alumina on silica gel has been noted previously [2]. A very small addition of Al_2O_3 played the part of activator in a nickel - silica gel catalyst that had been reduced with hydrogen for the polymerization of ethylene to liquid fuel at 350-450° and 2-10 atm [3]. Addition of 1.5% of alumina to a nickelous oxide - silica gel impregnation catalyst produced a threefold increase in the rate of polymerization of ethylene at 50-150° and 135 atm [4]. An NiO - aluminum silicate catalyst containing 2% of Al_2O_3 has been used in the polymerization of a 9 : 11 mixture of ethylene and hydrogen at 40° and 20 atm [5].

In the present work, in which ethylene was polymerized at 300° and atmospheric pressure, an investigation was made of the activities of nickelous oxide - silica gel catalysts promoted with alumina and prepared both by precipitation from the nitrate and by impregnation with nickel formate solution.

EXPERIMENTAL

The apparatus and experimental procedure were as before [1]. The duration of each experiment was five hours. Table 1 gives the results obtained with impregnation catalysts, the preparation of which is described below.

TABLE 1

Catalyst No.	Catalyst	Expt. No.	C ₂ H ₄ reacted, %	Butene yield (%)		Yield of higher hydrocarbons, %	
				on C ₂ H ₄ passed	on C ₂ H ₄ reacted	on C ₂ H ₄ passed	on C ₂ H ₄ reacted
78	NiO-Al ₂ O ₃ -ShSK	1	20,0	3,7	18,5	3,7	18,5
43	NiO-ShSK	1	0,0	0,0	0,0	0,0	0,0
71	NiO-Al ₂ O ₃ -KSK	1	71,4	34,9	48,8	29,3	41,1
71	NiO-Al ₂ O ₃ -KSK	2	46,0	29,1	52,0	8,5	18,4
60	NiO-KSK	1	31,3	25,4	81,0	6,0	19,2
60	NiO-KSK	2	17,8	12,6	70,5	1,6	9,2

Catalyst 78 was prepared by treatment of 10 ml of ShSK silica gel with 100 ml of 0.2 N aluminum nitrate solution at the boil for two hours. After being washed free from nitrate ions and dried for one hour at 120°, the silica gel was treated, as described previously [1], with boiling 1% nickel formate solution. After decantation the catalyst was dried at 120°. Before use it was heated in a stream of ethylene at 300°.

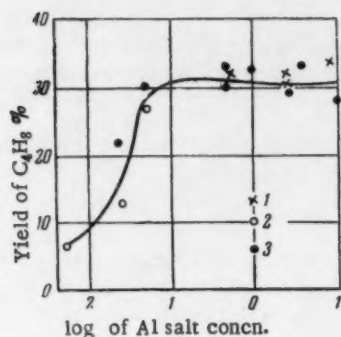


Fig. 1. Effect of the concentration of aluminum salt used in the preparation of the catalyst on the yield of butene (% on ethylene passed): 1) KSK (Sample 1); 2) KSK (Sample 2); 3) KSK (Sample 3).

Catalyst 71 was prepared by boiling 100 ml of a 2.5% solution of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ for two hours in presence of 10 ml of KSK silica gel (Sample 1). It was then impregnated with 1% nickel formate solution.

In Table 1, for comparison, we give data obtained with catalysts prepared analogously, but not containing alumina. All the experiments of Table 1 were carried out at a contact period of 11-13 seconds. Table 1 shows that the addition of alumina to NiO - ShSk silica gel, a catalyst which was quite inactive whether it was prepared from nickel nitrate or from nickel formate (Catalyst 43), produced some, even though feeble, activity (Catalyst 78). The results obtained over Catalysts 71 and 60, which contained KSK silica gel (Sample 1), show that the addition of alumina to such an NiO - KSK catalyst raises its activity both in dimerization and in the formation of liquid polymers. In the first five hours of work the amount of ethylene that reacted was raised from 31.3% to 71.4%, and in the second five hours from 17.8% to 46%. The yield of dimer rose correspondingly from 25.4% to 34.9% and from 12.6% to 29.1%, and the amount of higher hydrocarbons from 6.0% to 29.3% and from 1.6% to 8.5% on the ethylene passed.

It is interesting to note that impregnation catalysts that we examined which had alumina alone, common clay, white clay or Muslyumkin clay as carrier were quite inactive in the polymerization of ethylene. An analogous nickel catalyst on activated charcoal was also quite inactive. As is well known, the catalyst Co - activated charcoal actively promotes the polymerization of ethylene with formation of dimer in high yield [6]. It was found that NiO catalysts on kieselguhr and Georgian gumbrin were of low activity.

We investigated the effect of the concentration of aluminum salt in the solution used for the preparation of an impregnation $\text{NiO} - \text{Al}_2\text{O}_3$ - KSK catalyst on the activity of the catalyst. For the treatment of KSK silica gel we used aluminum nitrate solutions of various concentrations. The results are given in Table 2 and Fig. 1. All the catalysts were prepared in the same way. The experiments were carried out with a contact period of 5-6 seconds. Table 2 gives experiments with catalysts prepared from KSK (Sample 3).

TABLE 2

Catalyst No.	Concn. of $\text{Al}(\text{NO}_3)_3$ soln. (%)	Expt. No.	C_2H_4 reacted, %	Butene yield (%)		Yield of higher hydrocarbons, %	
				on C_2H_4 passed	on C_2H_4 reacted	on C_2H_4 passed	on C_2H_4 reacted
175	0.025	1	34.4	22.8	66.3	3.5	10.3
184	0.05	1-2	59.3-24.7	30.7-17.6	61.1-71.4	6.6-4.0	13.2-15.8
184	0.05	3-4	19.2-19.0	14.9-11.8	77.4-62.0	3.5-2.9	17.9-15.5
195	0.5	1-2	53.0-33.5	33.3-22.7	63.0-67.7	10.3-5.3	19.7-16.0
195	0.5	3-4	28.3-20.3	17.6-11.2	62.2-55.1	4.5-2.3	16.2-11.6
207	1.0	1-2	51.3-37.3	33.1-26.6	64.5-71.5	8.6-4.8	16.7-13.2
176	2.7	1-2	48.3-30.0	30.8-21.8	64.0-73.0	9.6-3.7	20.3-12.0
176	2.7	3-4	24.1-19.8	15.8-11.5	66.0-58.0	2.9-2.6	12.0-12.9
193	4.0	1-2	48.1-38.9	33.3-23.9	69.2-61.5	8.2-5.0	17.0-12.8
193	4.0	3-4	25.4-25.3	19.4-18.1	76.6-71.8	3.6-2.4	14.2-11.4
192	10.0	1-2	41.0-27.5	28.0-16.8	70.0-61.2	11.3-3.4	28.0-12.4
192	10.0	3-4	26.3-20.8	18.4-13.1	70.0-62.8	2.2-2.7	8.4-12.7

The results show that weak solutions of aluminum nitrate (0.05% and more dilute) are not suitable for the treatment of KSK silica gel because the catalysts obtained are of low activity. Solutions of 0.5–10% were found to be all equally suitable, and no particular difference was observed in the properties of the catalyst with change in the concentration of aluminum nitrate over this range.

Above we have described the results of an investigation of impregnation catalysts in the polymerization of ethylene. It was of interest to study some catalysts of the same kind, but prepared by precipitation from the nitrate solution. Alumina was introduced into the catalyst by the same impregnation method. The following catalysts were investigated; they were used in 5-ml portions:

Catalyst 81 was prepared by precipitation of a hot solution of 3.5 g of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and 4 g of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in 100 ml of water in presence of 10 ml of KSK silica gel and 50 ml of dilute ammonia.

Catalyst 83 differed from the previous catalyst in that alumina was not added.

Catalyst 232 was prepared as follows: 20 ml of silica gel was heated in a solution of 0.2 g of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ in 100 ml of water in a flask fitted with reflux condenser for one hour in a water bath. The product was washed free from nitrate ions and dried at 120° , and 10 ml was taken and heated at the boil in 10 ml of 20% $\text{Ni}(\text{NO}_3)_2$ solutions. This was followed by precipitation with potassium carbonate (5 g of K_2CO_3 in 25 ml of water; to an alkaline reaction) and heating at the boil was repeated. After the mixture had stood for 30 minutes, the solution was poured off, and the solid phase was washed free from nitrate ions and dried at 120° . The tube was loaded with 5 ml of the catalyst in a layer 6 cm long. Before use the catalyst was heated for one hour in a stream of air at 300° .

Catalysts 225 and 226 were prepared like the preceding catalysts, the only difference being the use of a saturated nickel nitrate solution and precipitation with a small excess of aqueous ammonia; the length of the layer was 7 cm.

Catalysts 227 and 228 were prepared like the preceding catalysts, the only difference being that the 20 ml of silica gel was first treated with a solution of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in 200 ml of water, with which it was heated in a water bath, and was then washed free from nitrate ions and dried at 120° . The length of the layer was 7 cm. Catalysts 81 and 83 were prepared from KSK silica gel, Sample 2, and the remainder were prepared from KSK Sample 3.

The results of experiments with these catalysts are given in Table 3. The contact period was 13–14 seconds in experiments with Catalysts 81 and 83 and 5.5–6.0 seconds in the other experiments. Table 3 shows that considerable increase in activity in the polymerization of ethylene is observed when alumina is added to an NiO–KSK catalyst prepared by precipitation from nickel nitrate solution with ammonia (Catalysts 81 and 83). The catalyst $\text{NiO} - \text{Al}_2\text{O}_3 - \text{KSK}$ prepared by precipitation with potassium carbonate was quite inactive (Catalyst 232), but that prepared by precipitation with ammonia was active. Over the latter the conversion of ethylene was 26–43% with initial yields of butene of 23–27% and of higher hydrocarbons of 3–5.3% on the ethylene passed. However, the catalyst could not be adequately regenerated, and its activity fell as the reaction proceeded. Addition of zinc oxide to this catalyst altered its properties; its regenerability was somewhat increased, and its selectivity with respect to dimerization was somewhat raised.

SUMMARY

1. Addition of alumina to an impregnation catalyst of NiO on KSK silica gel prepared from nickel formate has a strong activating effect on the catalyst for the polymerization of ethylene.
2. With change in the concentration of the aluminum nitrate solution used for the preparation of an $\text{NiO} - \text{Al}_2\text{O}_3 - \text{KSK}$ silica gel catalyst from 0.5% to 10% there is little change in the activity of the latter; lower concentrations give a catalyst of low activity.
3. Alumina, kieselguhr, various kinds of clay, and activated charcoal are not suitable as carriers for nickelous oxide as a catalyst for the polymerization of ethylene.
4. The precipitation catalyst $\text{NiO} - \text{Al}_2\text{O}_3 - \text{KSK}$ silica gel, prepared from the nitrate by precipitation with potassium carbonate is inactive, and that prepared by precipitation with ammonia is active, but of inadequate stability and regenerability. Addition of zinc oxide somewhat raises the regenerability and the selectivity with respect to the dimerization of ethylene.

Catalyst No.	Catalyst	Expt. No.	C ₂ H ₄ reacted, %	Butene yield (%)		Yield of higher hydrocarbons, %	
				on C ₂ H ₄ passed	on C ₂ H ₄ reacted	on C ₂ H ₄ passed	on C ₂ H ₄ reacted
81	NiO-Al ₂ O ₃ -KSK	1	34,4	22,0	64,0	3,4	10,1
83	NiO-KSK	1	12,7	7,6	58,0	3,3	25,4
232	NiO-Al ₂ O ₃ -KSK (pptd. with K ₂ CO ₃)	1	0,0	0,0	0,0	0,0	0,0
225	NiO-Al ₂ O ₃ -KSK (pptd. with ammonia)	1-2	43,0-29,5	27,0-18,7	63,0-63,6	5,3-2,7	12,1-9,0
225	The same	3*-4	26,8-18,0	15,0-10,0	55,8-56,0	2,8-2,3	11,2-14,0
225	"	5*	20,9	9,8	47,3	2,4	11,6
225	"	6*	20,0	13,0	66,7	2,0	10,3
225	"	7*	11,1	9,7	82,3	1,4	14,0
226	"	1-2	35,0-12,4	23,0-5,0	66,5-40,0	3,0-1,4	8,7-11,6
226	"	3*	20,6	13,9	67,5	2,4	11,7
226	"	4*	23,7	17,9	75,0	2,2	9,5
226	"	5*	13,0	7,4	55,0	0,7	5,4
227	NiO-ZnO-Al ₂ O ₃ -KSK	1-2	27,0-22,0	15,1-16,5	55,7-74,7	3,1-2,3	12,6-10,5
227	The same	3	14,6	6,6	45,4	1,5	10,0
227	"	4*	20,3	17,2	84,8	2,8	16,0
228	"	1-2	24,0-13,4	15,5-7,4	64,5-55,0	2,4-1,5	10,0-10,8
228	"	3*	27,8	16,3	58,8	2,9	10,5
228	"	4*	25,8	19,4	75,0	3,4	13,3

* Before this experiment the catalyst was regenerated in a stream of air at 450° for five hours.

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CATALYTIC HYDROCONDENSATION OF CARBON MONOXIDE WITH OLEFINS

COMMUNICATION 26. EFFECT OF ADDITIONS OF METAL OXIDES ON THE ACTIVITY OF A COBALT-KIESELGUHR (KISATIBI) CATALYST IN THE HYDROCONDENSATION OF CARBON MONOXIDE WITH ETHYLENE AND IN THE HYDROPOLYMERIZATION OF THE LATTER UNDER THE ACTION OF CARBON MONOXIDE

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Translated from *Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk* 1960,

No. 1, pp. 120-124, January 1960

Original article submitted May 21, 1958

The hydrocondensation of carbon monoxide with ethylene and other simple olefins and the hydropolymerization of olefins under the action of small amounts of carbon monoxide proceeds in presence of catalysts based on cobalt [1]. As already pointed out [2], the catalyst used originally contained ThO_2 as promotor (18% on the amount of metallic cobalt) and was supported on kieselguhr (kisatibi); the ratio by weight of cobalt to carrier was 1 : 1.

In the literature, statements are met to the effect that in mixed catalysts particular components determine the activity of the catalyst only in relation to certain stages of the complex catalytic process. Thus, the synthesis of higher hydrocarbons from carbon monoxide and hydrogen consists of a series of stages: hydrogenation of carbon monoxide to methylene radicals and of the olefins formed from them into paraffins, polymerization of methylene radicals into hydrocarbon chains, etc; it is supposed that in this complex process Group VIII metals (Co, Ni, Fe) bring about the hydrogenation and the difficulty reducible oxide promotor (ThO_2 , MnO , Al_2O_3) brings about the condensation [3]. There is only a certain amount of truth in such views, because in all stages the catalyst acts as a unified whole, and its separate components do not possess so much independence, though they may and must play an important part in joint action with other components. The removal of a component or change in the relative amounts of components does indeed lead to a change in the properties of the whole catalyst. In this connection it was of interest to investigate the effect of the nature of the components of the catalyst and also of various new additions on its condensing and hydrogenating properties. The possibility of raising or lowering the condensing power of a catalyst is also of practical importance. Thus, an interesting possibility would be the stopping of hydropolymerization at a definite stage, e.g. that of the dimer or trimer. This applies to ethylene when it is desirable to obtain high yields of the butane-butene fraction, which is of practical interest from many points of view. The same can be said of the possibility of changing the hydrogenating power of the catalyst. To a first approximation, in experiments with ethylene a sufficient criterion of the lowering of the condensing power of the catalyst is provided by the increase in the relative yield of $\text{C}_3 + \text{C}_4$ fraction (gas oil), account being taken of the fact that there is also an increase in the amount of dissolved original ethylene and ethane in this fraction.

In the present work we investigated the activity of an unpromoted Co-kieselguhr (kisatibi) catalyst in the hydrocondensation of carbon monoxide with ethylene and the hydropolymerization of the latter under the action of small amounts of carbon monoxide, and we investigated also the effect of additions of metal oxides other than ThO_2 on this activity. As additive we tried magnesium, vanadium, manganese, and aluminum oxides.

TABLE 1

Characterization of the Activity of Unpromoted Co - Kieselguhr (Kisatibi)
Catalyst

Catalyst	Time in work (hr)	Space velocity (hr ⁻¹)	Gas contraction, (%)	Yield of hydrocarbons (total) (ml/m ³)	Yield of gas oil (ml/m ³)
18	10	200	56	280	113
18	15	200	56,5	364	202
19	5	160	59	353	176
19	15	100	58	316	103
19	4	200	56	285	102

EXPERIMENTAL

The apparatus and experimental procedure have been described previously [1]. The reaction vessel consisted of a glass tube, 10 mm in diameter, in which the catalyst sample was placed in a layer 30-45 cm long. The tube was placed in a furnace with an automatic thermoregulator which maintained the temperature constant within $\pm 1.5^\circ$. Ethylene was prepared by the dehydration of ethanol over alumina and was purified by passage through concentrated sulfuric acid, caustic alkali solution, and tubes containing solid potassium hydroxide and activated charcoal. The experiments were carried out at 190-200° and atmospheric pressure in a flow system with overnight interruptions; the original mixture had $C_2H_4 : H_2 = 1 : 0.8-1$ and contained 5-6% of CO. The space velocity was 100-120 hour⁻¹. The catalysts were prepared by precipitation with potassium carbonate from solutions of nitrates in presence of kieselguhr (kisatibi), and they contained 5 g of Co. The length of the catalyst layer in the reaction tube was 30-35 cm. Before use the catalysts were reduced with hydrogen at 400-450°. They were regenerated with hydrogen at 450° for three hours. The reaction products were trapped in two receivers: In the first, which was at room temperature, a lower aqueous and an upper oily ("heavy oil") layer collected; in the second, which was at -80°, "light oil" condensed. The results are given in Tables 1-4.

DISCUSSION OF EXPERIMENTAL RESULTS

Co - Kieselguhr (Kisatibi) (1 : 1). Catalysts 18 and 19 were reduced with hydrogen at 450° for five hours, as were all subsequent catalysts in this section of the work. The results are given in Table 1, which shows that the total yield of hydrocarbons, including gas oil, was 300-350 ml/cu.m. At a space velocity of 100 hour⁻¹ the productivity of the catalyst was 31-33 ml/liter·hour. Increase in the space velocity to 200 hour⁻¹ raised the productivity to 67-68 ml/liter·hour. More than 50% by volume of the condensate was gas oil. From the values of the contraction (56-59%) and the analyses of the original and final gases it follows that 60-70% of the ethylene that reacted was converted into ethane. The extents of reaction were: ethylene 92-98%, hydrogen 88-94%, and carbon monoxide 50-75%.

TABLE 2

Characterization of the Activity of a Co - MgO - Kieselguhr (Kisatibi)
Catalyst

Catalyst	Time in work (hr)	Space velocity (hr ⁻¹)	Gas contraction (%)	Yield of hydrocarbons (total) (ml/m ³)	Yield of gas oil (ml/m ³)
20	10	94	60,6	265	66
20	15	96	61,7	353	125

It will be seen from the results that an unpromoted Co - kieselguhr (kisatibi) catalyst has high hydrogenating and low condensing powers. The formation of hydrocarbons from carbon monoxide, hydrogen, and ethylene occurs, but the predominating reaction is the hydrogenation of ethylene to ethane (up to 70% of the ethylene that reacts). Below we give the compositions of the original and final gases (% by volume) in two separate experiments:

The gas contractions were 56.9% and 62.2%, respectively.

Co - MgO - Kieselguhr (Kisatibi)

(1 : 0.16 : 1). It is known [4] that magnesium oxide is used as a promotor of a cobalt-kieselguhr catalyst (together with ThO₂) in the preparation of a commercial catalyst for the synthesis of hydrocarbons from carbon monoxide and hydrogen. It

was of interest to try magnesium oxide as a promotor in a catalyst for the hydrocondensation of carbon monoxide with olefins and their hydropolymerization under the action of carbon monoxide. With this object we prepared Catalyst 20 (Table 2). Over this catalyst up to 70% of the ethylene that reacted was hydrogenated to ethane.

Example of compositions of original and final gases (% by volume:

	C ₂ H ₄	H ₂	CO	C ₂ H ₆	CO ₂
Original gas	45,0	50,2	4,8	0,0	0,0
Final gas	2,5	5,9	0,0	88,4	3,2

The gas contraction was 64.8%.

The results show that MgO does not promote a Co - kieselguhr (kisatibi) catalyst. The properties of the latter were scarcely altered by the addition of MgO.

TABLE 3

Characterization of the Activity of Co - V₂O₅ - Kieselguhr (Kisatibi)
Catalysts

Catalyst	Time in work (hr)	Space velocity (hr ⁻¹)	Gas contraction (%)	Yield of hydrocarbons (total) (ml/m ³)	Yield of gas oil (ml/m ³)
21	40	160	62	386	148
22	30	165	61	410	146

Co - V₂O₅ - Kieselguhr (Kisatibi). The promoting effect of vanadium oxide on a Co - kieselguhr (kisatibi) catalyst was tried on two samples; Catalysts 21 and 22. Catalyst 21 was prepared by precipitation from cobalt nitrate solution with potassium carbonate in presence of kieselguhr (kisatibi) with subsequent impregnation with ammonium vanadate and reduction in the usual way. Its composition was Co : V₂O₅ : kisatibi = 1 : 0.02 : 1. Catalyst 22 differed from Catalyst 21 only in the proportions of the components, which were 1 : 0.06 : 1. The results are presented in Table 3.

TABLE 4

Characterization of the Activity of a Co - MnO - Al₂O₃ - Kieselguhr (Kisatibi)
Catalyst

Catalyst	Time in work (hr)	Space velocity (hr ⁻¹)	Gas contraction (%)	Yield of hydrocarbons (total) (ml/m ³)	Yield of gas oil (ml/m ³)
23	15	100	58	267	62
23	5	81	28	73	9

On the average the ethylene reacted to the extent of 97%, and 50-55% of ethylene that reacted was hydrogenated to ethane. Hydrogen reacted to the extent of 70-75%, and carbon monoxide to the extent of 65-70%.

Comparison of Tables 1 and 3 shows that vanadium oxide has a definite promoting action. At equal space velocities of gas at the catalyst containing the promoter, the average yield of condensate was increased by about 50 ml/cu·m, or 10 ml/liter·hour. The condensing power of the catalyst was increased (the relative yield of gas oil fell), and its hydrogenating power was reduced (the yield of ethane fell).

Co - MnO - Al₂O₃ - Kieselguhr (Kisatibi) (1 : 0.2 : 0.6 : 1). It is known that a combination of manganese and aluminum oxides acts as a promotor for the "normal" nickel catalyst in the synthesis of hydrocarbons from carbon monoxide and hydrogen [5]. We applied this combination in the Co - kieselguhr (kisatibi) catalyst for the formation of hydrocarbons from carbon monoxide, hydrogen, and ethylene. Catalyst 23 was prepared by the usual coprecipitation from a solution of cobalt, manganese, and aluminum nitrates with subsequent reduction with hydrogen at 450° for five hours. The results are shown in Table 4. The ethylene reacted to the extent of 87-94%, carbon monoxide to the extent of 71-77%, and hydrogen to the extent of 84-91%. Up to 70% of the ethylene that reacted was hydrogenated to ethane. The results show that the introduction of manganese and aluminum oxides leads to a lowering of the activity and stability of a Co - kieselguhr (kisatibi) catalyst. After 15 hours in work the activity of the catalyst fell sharply. Hence, a Co - MnO - Al₂O₃ - kisatibi catalyst was of low efficiency.

From a comparison of the catalytic properties of a Co - ThO₂ - kieselguhr (kisatibi) catalyst and those of the corresponding unpromoted catalyst, the function of ThO₂ as a promotor emerges particularly clearly: increasing the condensing power and lowering the hydrogenating powers of the Co - kieselguhr catalyst. The unpromoted catalyst had high hydrogenating power, which is evident from the fact that up to 70% of the ethylene that reacted was converted into ethane. Magnesium oxide does not possess these properties, and on its addition the hydrogenating activity of the catalyst is not reduced, but vanadium oxide does possess them, but to a less extent. The joint addition of manganese and aluminum oxides, which is usual for a normal nickel catalyst, lowers the activity of a Co - kieselguhr catalyst for the hydrocondensation of CO with C₂H₄ and the hydropolymerization of the latter under the action of CO.

SUMMARY

1. The effect of additions of metal oxides on the activity of a Co - kieselguhr (kisatibi) catalyst was investigated. When this catalyst does not contain these additions it is active in the hydrocondensation of carbon monoxide with ethylene and the hydropolymerization of the latter under the action of carbon monoxide. However, the hydrogenating power of the catalyst is very high.
2. A study was made of the promoting effects of various oxides on a Co - kisatibi catalyst. Addition of magnesium oxide scarcely affects the catalytic properties of this catalyst, and the joint addition of manganese and aluminum oxides leads to a reduction in activity and a sharp fall in the catalytic stability of the catalyst.
3. Vanadium oxide has an activating effect on a Co - kisatibi catalyst.

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* Original Russian pagination. See C.B. Translation.

BRIEF COMMUNICATIONS

TRANSFORMATIONS OF DIISOBUTYLENE (2,4,4-TRIMETHYL-1-PENTENE) UNDER THE CONDITIONS FOR THE DESTRUCTIVE HYDROPOLYMERIZATION OF ISOBUTENE

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Translated from *Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk* 1960,

No. 1, pp. 125-127, January 1960

Original article submitted April 27, 1959

It was shown previously [1, 2] that an equimolecular mixture of isobutene and hydrogen, passed over a Co-clay catalyst at 190° under atmospheric pressure, undergoes a peculiar transformation, which was described as the destructive hydropolymerization of isobutene. After its complete hydrogenation, the reaction product consisted mainly of a mixture of 2-methylalkanes (2-methylbutane, 2-methylpentane, etc.) and contained none of the true isobutene polymers, "diisobutylene" and "triisobutylene", and their hydrogenation products, which predominate in the reaction products when the original mixture contains less hydrogen, e.g. 25% of hydrogen and less.

The course of the destructive hydropolymerization of isobutene may be represented as follows: True polymerization of isobutene first occurs with formation mainly of diisobutylene and its hydrogenation product (a C₈ paraffin) and these under the action of hydrogen undergo hydrocracking and disproportionation. Another possible course consists of the reaction of alkyl radicals formed by the hydrocracking of isobutene dimers and trimers with the original isobutene. And finally, a third possible course: hydrocracking of isobutene with formation of methyl and other radicals, which react further with isobutene molecules adsorbed on the catalyst. To elucidate this matter it was of interest to investigate the behavior of diisobutylene under the conditions for the destructive hydropolymerization of isobutene. We here report the results of such an investigation with the α -isomer of diisobutylene (2,4,4-trimethyl-1-pentene).

TABLE

Expt.	Molar ratio H ₂ : C ₈ H ₁₆ in original vapor- gas mixture	Over-all space vel- ocity of original vapor-gas mixture	Yield of catalyzate (% by vol. on original C ₈ H ₁₆)	Content of unsaturateds in catalyzate (%)	Yield of C ₅ -C ₇ hydrocracking products in catalyzate
1	1,8	116	100	14	15,4
2	8,7	109	89,7	1,5	18,7
3	10,7	184	95	0,0	20,8
4	13,9	172	96,0	0,0	17,5
5	1,2*	93	101,7	72,4	9,0

* In this experiment isobutene was passed together with H₂ and C₈H₁₆; the ratio H₂ : C₈H₈ was 1 : 1.

EXPERIMENTAL

The apparatus and experimental procedure have been described previously [1-3]. Diisobutylene was synthesized by Butlerov's method [4] by the polymerization of isobutene under the action of 63% sulfuric acid, and it was purified from traces of sulfur trioxide and oxidation products by distillation over sodium. Fractionation through a column having a filling of copper triangular spirals and giving an efficiency of 40 theoretical plates gave a fraction of b.p. 101-102° (760 mm), n_D^{20} 1.4100, d_4^{20} 0.7158. For 2,4,4-trimethyl-1-pentene the literature [5] gives b.p. 101.36°, n_D^{20} 1.4086, and d_4^{20} 0.7150. In the experiments we used the Co-clay catalyst usually used for the hydrocondensation of carbon monoxide with olefins; 30 ml of it was loaded into the glass reaction tube (diameter 10 mm), and before each experiment it was regenerated with electrolytic hydrogen at 430° for five hours. Diisobutylene was fed into the reaction tube from an automatic buret. All experiments were carried out at atmospheric pressure and 190°. The duration of an individual experiment was 10-20 hours. The liquid catalyzates from each experiment were dried and fractionated through the above-mentioned column, and the residues, which boiled above 125°, were distilled from a Wurtz flask. The results are given in the table and in Figs. 1 and 2.

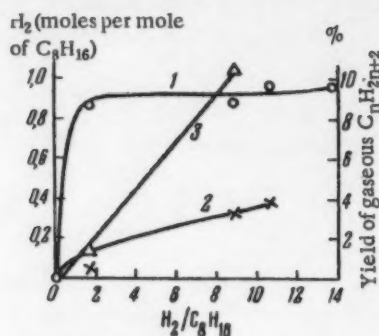


Fig. 1. Relation of the amounts of H_2 (moles per mole of original C_8H_{16}) consumed in hydrogenation (Curve 1) and in hydrocracking (Curve 2), and of the yield (%) of gaseous cracking products (Curve 3), to the $H_2 : C_8H_{16}$ ratio in the original vapor-gas mixture.

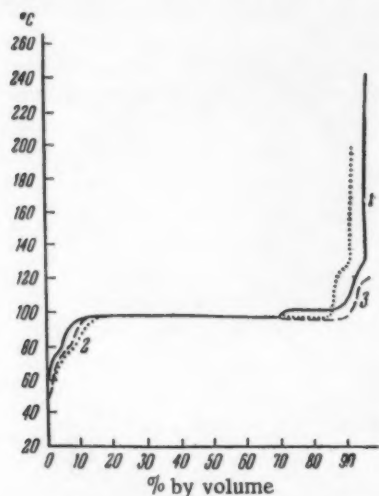


Fig. 2. Fractionation curves of catalyzates: 1) Expt. 1; 2) Expt. 2; 3) Expt. 4.

In the experiments the $H_2 : C_8H_{16}$ ratio was varied over a wide range: from 1.8 to 13.9. Such a large excess of hydrogen was taken because it was considered that in the destructive hydropolymerization of isobutene the hydrocracking of diisobutylene may occur as soon as it is formed, i.e. when there is a large excess of hydrogen. It was found that the main reaction was the hydrogenation of diisobutylene into the C_8 paraffin, and this was the more complete the greater the $H_2 : C_8H_{16}$ ratio. At high values of this ratio (Experiments 2 and 3) catalyzates were obtained which did not contain unsaturated hydrocarbons. To some extent skeletal isomerization of the diisobutylene or C_8 paraffin occurred. The content of isomeric C_8 hydrocarbons (fraction of b.p. 105-125°) in the liquid catalyzates was 5-8%. Hydrocracking went to an appreciable extent with formation of C_5-C_7 hydrocarbons (fraction of b.p. below 98°), and with an excess of hydrogen in the vapor-gas mixture the content of these in the catalyzates was 15-20%. It must be pointed out that increase in the $H_2 : C_8H_{16}$ ratio from 1.8 to 13.5 had extremely little effect on the yield of liquid hydrocracking products (Fig. 1, Curve 2). The yield of gaseous hydrocracking products (methane) attained a maximum of 10.4% (Fig. 1, Curve 3) on the amount of diisobutylene passed; the content of C_9 and higher hydrocarbons in the catalyzates did not exceed 7.6%.

Examination of the results shows that, under the action of hydrogen under the given conditions, 2,4,4-trimethyl-1-pentene is mainly hydrogenated with formation of 2,4,4-trimethylpentane (i.e. 2,2,4-trimethylpentane). Skeletal isomerization, hydrocracking, and molecular disproportionation occur to a small extent and, what is particularly important, the formation of C_5-C_7 hydrocarbons remains almost constant at 18-20% over a wide range of $H_2 : C_8H_{16}$ ratios (1.8 - 13.5). These results show that 2-methyl hydrocarbons obtained in the destructive hydropolymerization of isobutene are not formed by the destructive hydrogenation of diisobutylene. The results of Expt. 4 with a

ternary mixture of hydrogen isobutene, and 2,4,4-trimethyl-1-pentene showed that the formation of these 2-methyl hydrocarbons can also not be explained by the reaction of alkyl radicals formed in the hydrocracking of 2,4,4-trimethyl-1-pentene with isobutene. It must probably be ascribed to the occurrence first of hydrocracking of isobutene at the catalyst surface and further reaction of the decomposition products (alkyl radicals) with adsorbed isobutene molecules.

SUMMARY

1. Under the action of hydrogen in presence of a Co-clay catalyst at atmospheric pressure and 190°, 2,4,4-trimethyl-1-pentene is mainly hydrogenated to 2,2,4-trimethylpentane. Skeletal isomerization, hydrocracking, and molecular disproportionation occur only to a small extent over a wide range of $H_2 : C_8H_{16}$ ratios.

2. It is suggested that the formation of 2-methyl hydrocarbons during the destructive hydropolymerization of isobutene proceeds via the hydrocracking of isobutene and reaction of the decomposition products (alkyl radicals) with adsorbed isobutene molecules.

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* Original Russian pagination. See C. B. Translation.

DEHYDRATION OF TETRAHYDRO-2-METHYLPYRAN OVER A TITANIA-ALUMINA CATALYST

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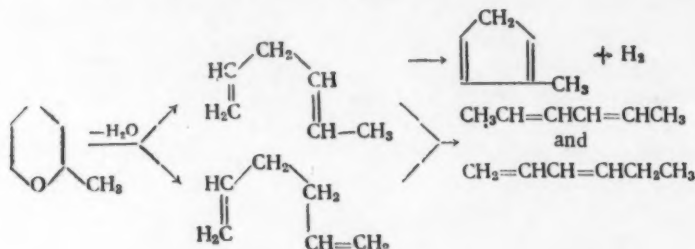
Translated from *Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk* **1960**,

No. 1, pp. 127-129, January 1960

Original article submitted May 25, 1959

The catalytic transformations of compounds of the tetrahydropyran series have been inadequately studied. Only investigations on the isomerization of homologs of tetrahydropyran over platinized charcoal [1] and the transformations of dihydropyran over nickel [2], aluminum silicate, phosphate, and oxide [3] catalysts have been reported. We decided to investigate the dehydration of tetrahydro-2-methylpyran. Recently [4] one of us showed that, in the dehydration of 2-ethyltetrahydrofuran over TiO_2 at 600° under reduced pressure, the products included not only 1,3-hexadiene, methylcyclopentadiene, and benzene, but also 1,3-cyclohexadiene, the content of which in the $78-80^\circ$ fraction (66% yield) attained 40% in some experiments. In view of this we expected to obtain analogous results in the dehydration of tetrahydro-2-methylpyran.

For the elimination of the elements of water we passed the tetrahydro-2-methylpyran over $\text{TiO}_2-\text{Al}_2\text{O}_3$ (8 mole percent of Al_2O_3) at 450° , 500° , and 600° at reduced pressure (25-30 mm) at a space velocity of 0.2-0.3 hour⁻¹. However, under these conditions no 1,3-cyclohexadiene was detected in any of the catalyzates. At 600° a large amount of a fraction of b.p. $79-80^\circ$ was obtained; it consisted of benzene and 2,4-hexadiene with a little methylcyclopentadiene. The main product in these transformations was 2,4-hexadiene, the content of which was 34% in the catalyzate from the experiment carried out at 450° . The total content of conjugated dienes varied from 27% in the experiment at 600° to 44% in the experiment at 450° . The yield of conjugated dienes in the dehydration of tetrahydro-2-methylpyran was considerably less than in the analogous transformations of compounds of the tetrahydrofuran series. This is probably associated with the fact that the dehydration product first formed is in this case an unconjugated diene, which then isomerizes to a conjugated system:



EXPERIMENTAL

Tetrahydro-2-methylpyran was prepared by Paul's method [5] and had the following properties: b.p. 102.9° (762 mm); d_4^{20} 0.8566; n_D^{20} 1.4193. The catalyst was prepared by grinding a mixture of titanium dioxide with precipitated aluminum hydroxide and roasting it at 600° ; it was molded into 4 x 4-mm cylinders.

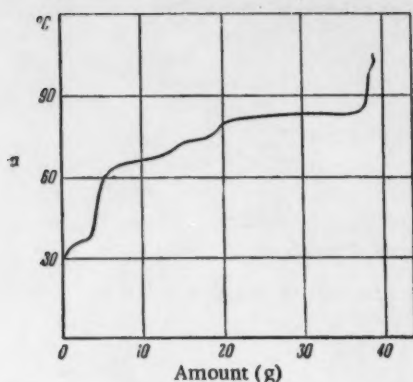


Fig. 1. Fractionation curve for the catalyzate from Expt. 1, which was carried out at 450°; the fractionation curves for the catalyzates from the other experiments are similar.

172–173° (Alder [6] gives m.p. 176° for this acid). 2,4-Hexadiene; b.p. 82–83° (760 mm); d_4^{20} 0.7251; n_D^{20} 1.4550; the adduct with maleic anhydride melted at 93–94° (the literature gives m.p. 93° [6] for the adduct of 2,4-hexadiene with maleic anhydride).

The light fractions (26–45°) from the catalyzates of all three experiments were combined; the bromination of the mixture gave a substance of m.p. 115.8°, which corresponds to piperylene tetrabromide. The literature [7] gives m.p. 114–115° for 1,2,3,4-tetrabromopentane. From another portion of this combined fraction we obtained an adduct with maleic anhydride which melted at 161°; it was the cyclopentadiene adduct [8].

TABLE

Transformations of Tetrahydro-2-Methylpyran over $TiO_2-Al_2O_3$

Expt.	Temp (°C)	Pressure (mm)	Space velocity (hr ⁻¹)	Yield of cata- lyzate (%)	Content (%) in catalyzate of						
					pentane, pentenes, 1,3- pentadiene, and cyclo- pentadiene	hexenes	1,4 and 1,5- hexadienes	1,3- hexadiene	2,4- hexadiene	benzene	methylcyclo- pentadiene
1	450	30	0,2	87,6	9,8	5,1	15,4	9,7	33,9	5,3	~0,5
2	500	30	0,2	77,3	10,4	16,6	10,3	23,3	9,7	1,0	
3	600	90	0,3	58,6	12,1	4,8	5,9	3,3	21,6	27,6	2,3

For all the remaining fractions the contents of conjugated dienes were determined [9]. The approximate proportions of hexenes and unconjugated hexadienes in their mixtures were determined from the iodine value. Methylcyclopentadiene was determined colorimetrically [10]. The benzene contents of the 73.4–79° and 79–81.5° fractions were found by difference after the determination of the conjugated dienes, for no other unsaturated hydrocarbons were found. Parallel analyses were carried out on all fractions with the aid of the Raman spectra.

SUMMARY

1. An investigation was made of the transformations of tetrahydro-2-methylpyran under the conditions of its dehydration over a titania-alumina catalyst under reduced pressure at 450°, 500°, and 600°.

The experiments were carried out in a catalysis tube of internal diameter 16 mm in which 100 ml of the catalyst was placed. The substance was fed from an automatic buret. The reaction products were collected in a water-cooled receiver and in two traps, the first of which was cooled with a mixture of methanol and solid carbon dioxide, while the second was cooled with liquid nitrogen. After the passage of 50 ml of substance the catalyst was always regenerated by oxidation in a stream of air at 600° for four hours. The catalyzate was separated from water by salting out, dried over anhydrous potassium carbonate, and distilled through a column of 40-plate efficiency. The main results are presented in the table.

1,3- and 2,4-Hexadienes were isolated as narrow fractions on the basis of the features of the corresponding plateaus on the precision-fractionation curve (Fig. 1), and they had the following constants: 1,3-Hexadiene; b.p. 72–74° (758 mm); d_4^{20} 0.7140; n_D^{20} 1.4399; the acid obtained by hydrolysis of its adduct with maleic anhydride melted at

2. The main dehydration product of tetrahydro-2-methylpyran was 2,4-hexadiene, which was accompanied by other hexadienes, in particular 1,3-hexadiene. Some cyclic hydrocarbons (benzene, methylcyclopentadiene, and cyclopentadiene) were also found in the catalyzates.

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*Original Russian pagination. See C. B. Translation.

ALKYLATION OF PROPANE AND ISOPENTANE WITH ETHYLENE UNDER PRESSURE AT HIGH TEMPERATURES

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Translated from *Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk* 1960,

No. 1, pp. 129-131, January 1960

Original article submitted June 2, 1959

It was previously shown [1-3] that the reactivity of saturated hydrocarbons to alkylation by propene is about the same for butane, pentane, and heptane. Propane was exceptional [2]: in its alkylation by propene the conversion of the latter was one-half as much (43 %) and the yield of alkyl derivatives was lower on the amount of propene taken and their unsaturation was higher than, for example, in the reaction of butane with propene [1].

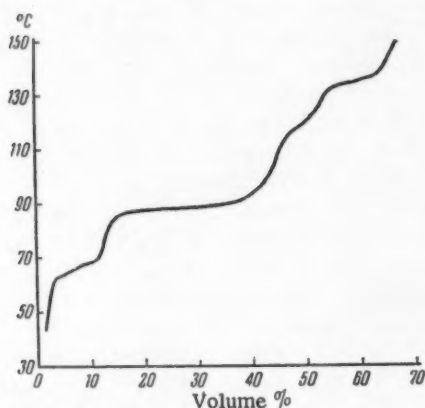


Fig. 1. Fractionation curve of the alkylation product obtained from isopentane and ethylene (Expt. 2).

20% of a 2 : 1 mixture of cis- and trans-2-pentenes. Hence, in the first stage ethylene attacks propane mainly at the secondary C atom, and only to a smaller extent at the primary carbon. Under the conditions of thermal alkylation [5] at 505° and 300 atm the C₅ fraction again consists mainly of isopentane; pentane is formed in smaller amount.

The results of the investigation of the composition of the C₇ fraction (85-95°) were particularly interesting; it formed 9-15% of the weight of alkylation product, and 75% of it came over in the range 88-90°. After removal of unsaturated hydrocarbons by chromatography on silica gel the fraction had d_4^{20} 0.6840 and n_D^{20} 1.3882. Analysis of the Raman spectrum showed that it contained 15% of 3,3-dimethylpentane [$\Delta \nu$ (cm⁻¹): 695(2); 707(1); 1447(3); and 85% 2-methylhexane [$\Delta \nu$, cm⁻¹: 308(3); 414(1); 434(1); 729(0); 784(1); 823(2); 874(1); 894(2); 890(0); 956(1); 1062(1); 1079(1); 1172(1); 1304(2); 1337(1); 1440(4); 1444(1); 1461(4b)].

In continuation of this investigation we have now studied the alkylation of propane with ethylene in presence of commercial alumina at 450° and 450-500 atm. The experimental method and the analysis were described previously [1]. It follows from Table 1 that the yield of C₅ fraction (up to 38°) in experiments with three alumina samples of different origin was low (9-12% of the weight of alkylation product). In the alkylation of butane with ethylene under similar conditions the alkylation product contained 37.3% of the expected C₅ fraction [4]. Table 1 shows that 70% of the C₅ fraction of the alkylation product boiled below 30°, and the remainder in the range 30-38°. The fraction of b.p. 25-30°, d_4^{20} 0.6292, and n_D^{20} 1.3550 consisted wholly of isopentane, which was identified from the characteristics of the Raman spectrum: $\Delta \nu$ (cm⁻¹): 461(4); 757(2); 764(10); 796(7); 909(2b); 954(1); 1014(1b); 1035(2); 1147(1); 1178(1); 1337(1); 1446(3); 1462(3). The fraction of b.p. 33-38°, d_4^{20} 0.6322, n_D^{20} 1.3642 contained 80% of pentane [$\Delta \nu$ (cm⁻¹): 401(5); 766(0); 840(2); 867(1); 1073(1); 1442(5); 1442(5); 1462(5)] and

TABLE 1

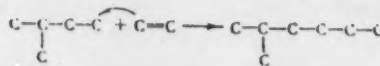
Alkylation of Propane with Ethylene at 450° in Presence of Alumina*

Expt.	Pressure (atm)	C ₂ H ₄ con- tent of origi- nal mixture wt. %	Space velocity** of C ₂ H ₄ (%)	Yield of alkylation product(% by wt. on ethyl- ene taken)	Fractional characterization of alkylation product							Content of higher- boiling residues		
					to 30°			30-38°		38-85°			85-95°	
					wt. %	bromine value	wt. %	bromine value	wt. %	bromine value	wt. %		bromine value	
1	450	13.3	1000	86	8,2	46	4,1	10,5	77	9,7	25	67,5		
2	500	18.4	1660	102	5,8	14	2,2	12,1	44	11,5	42	68,0		
3	500	16.4	850	75	6,4	13	2,6	15,0	46	15,4	15	60,6		
4	300	12.0	—	—	Bromine value of alkylation product ³¹									

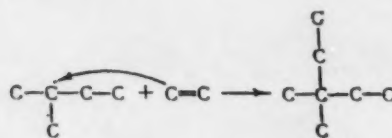
* In Expt. 1, a commercial sample of alumina; in Expt. 2, alumina treated successively with potassium fluoborate and sulfuric acid [2]; in Expt. 3, alumina impregnated with 1% of K₂CO₃.

** In liters of gas per liter of catalyst per hour.

Hence, in the second stage ethylene mainly attacks the primary C atom at the unbranched end of the isopentane molecule:



only to a small extent does it attack the tertiary C atom:



In this connection we carried out experiments on the alkylation of isopentane with ethylene. The original isopentane had b.p. 27.5° and n_D^{20} 1.3550. The results of these experiments are given in Table 2.

The alkylation product of Expt. 2 had a bromine value of 53, and its 85-95° fraction had a bromine value of 10. From the fractionation curve of the alkylation product of Expt. 2 (Fig. 1) it is seen that most of the C₇ fraction came over at 87-90°. After removal of unsaturated hydrocarbons by chromatography on silica gel it came over almost completely at 86.2-86.5° and had d_4^{20} 0.6929 and n_D^{20} 1.3910. In the Raman spectrum we found the following $\Delta \nu$ (cm⁻¹): 347(1); 374(1); 695(7); 707(2); 856(1); 913(1); 934(1); 1005(1); 1015(1); 1037(1); 1081(1); 1196(1); 1220(1); 1240(0); 1447(6); 1468(6). This shows that it consisted entirely of 3,3-dimethylpentane. We isolated also the product of the second stage of the alkylation of isopentane with ethylene. The fraction of b.p. 132-139° (8% on the weight of the alkylation product) was freed from unsaturated hydrocarbons and then had d_4^{20} 0.7338 and n_D^{20} 1.4132 (Fig. 1). Its Raman spectrum contained the following $\Delta \nu$ (cm⁻¹): 305(1); 725(2b); 884(1); 939(1); 1023(0b); 1060(1); 1104(1); 1200(1); 1452(5b); 1472(5b). This corresponds to 3,3-dimethylheptane.

We see that, as in the case of isobutane [6], in the first stage of alkylation ethylene attacks mainly the tertiary carbon atom, whereas at the second stage attack is mainly at a primary carbon atom. Analogously, in the reaction of butane with ethylene [4] in the first stage 3-methylpentane is obtained, which alkylates further at a primary carbon atom with formation of 3-methylheptane.

TABLE 2

	Expt.	
	1	2
Temperature (°C)	450	450
Pressure (atm)	450	450
Ethylene content of original mixture (% by wt.)	10.7	15.0
Space velocity (liters of liquid per liter of catalyst per hour)	2.0	1.77
Yield of alkylation product (% on wt. of ethylene taken)	150	175
Content of C ₇ fraction (85-95°) in alkylation product (% by wt.)	21.6	23.0

The result confirms our view that in the second stage it is not, for the most part, the hydrocarbon formed that is alkylated, but its intermediate form.

It should be noted that in the alkylation of isopentane with ethylene in presence of small amounts of organic halogen compounds 3,3-dimethylpentane was again obtained [7].

A. I. Palii took part in this work.

SUMMARY

1. The first stage of the alkylation of propane with ethylene leads mainly to the formation of isopentane, and to a smaller extent to the formation of pentane. The further alkylation (second stage) proceeds mainly at the primary carbon atom of the unbranched end of the isopentane molecule, and to a smaller extent at the tertiary carbon atom. On the other hand, when isopentane is taken and alkylated with ethylene, reaction is only at the tertiary carbon atom.

2. Propane is more difficult to alkylate with ethylene (and also with propene) than n-alkanes of higher molecular weight, and this is probably to be explained by the peculiarities of its structure.

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*Original Russian pagination. See C. B. Translation.

ISOMERIZATION OF SOME DIENE HYDROCARBONS
IN THE PRESENCE OF CALCIUM AMIDE

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Translated from *Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk* 1960.

No. 1, pp. 132-133, January 1960

Original article submitted June 9, 1959

As we have shown previously, calcium amide catalyzes the displacement of double bonds in mono- and diolefinic hydrocarbons [1-2]. Thus, diolefins containing isolated double bonds (1,5-hexadiene, 2-methyl-1,5-hexadiene, and 2,5-dimethyl-1,5-hexadiene) were readily isomerized in presence of calcium amide to diolefins containing a conjugated system of double bonds [1].

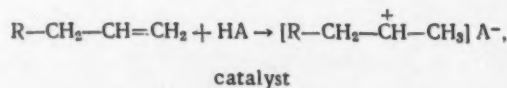
In the present work we investigated the effect of the structure of the diene on the rate of isomerization for the above-mentioned dienes. The isomerization was carried out in a flow system at 70° at a space velocity of 0.2. The properties of the original dienes and of their transformation products, and also the conversion calculated from change in refractive index and density, are given in the table. For comparison, in the same table we give the results of Henne and Turk [3] on the isomerization of these dienes in presence of alumina under the same conditions at 365°.

TABLE

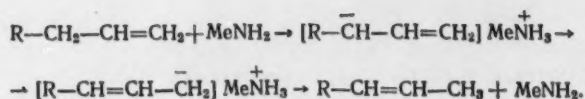
Original diene	Properties of diene		d_4^{20}	Properties of catalyzate		Degree of isomerization (%)	
	b.p. °C	n_D^{20}		n_D^{20}	d_4^{20}	Ca(NH ₂) ₂	Al ₂ O ₃
CH ₂ =CH-CH ₂ -CH=CH ₂	59,7	1,4038	0,6935	1,4388	0,7164	72	39
CH ₂ =C(CH ₃)-CH=CH ₂	88,1	1,4192	0,7190	1,4570	0,7314	77	58
CH ₂ =C(CH ₃)-CH ₂ -C(CH ₃)=CH ₂	113,9	1,4299	0,7419	1,4714	0,7593	84	81

It follows from these results that the relative rates of isomerization of the dienes vary very little in the case of calcium amide, but vary greatly in the case of alumina.

The difference in the behaviors of these dienes in presence of calcium amide, which has a basic character, and alumina, which is generally considered to have acidic properties, may be explained by a difference in the mechanisms by which these catalysts act. According to the most generally accepted view on the mechanism of the isomerization of olefins in presence of acidic catalysts, intermediate carbonium ions are formed:



and their formation is affected favorably by electron-donating methyl groups at the double bond, so that the rate of isomerization of 2,5-dimethyl-1,5-hexadiene is much higher than that of 1,5-hexadiene. The isomerization of olefins under the influence of metal amides probably occurs via the formation of carbonium ions by the elimination of protons [2]:



It is known that in olefins the highest mobility is possessed by hydrogen atoms in the allyl position and that the mobility of allyl hydrogen falls from the methyl to the methylidyne group $\text{CH}_3 > \text{CH}_2 > \text{CH}$ [4]. As the allyl hydrogen atoms are in methylene groups in all three dienes investigated, the possibility of the removal of a proton is approximately the same for all three dienes, so that the rates of their isomerization in presence of calcium amide are nearly the same.

SUMMARY

1. The relative rates of isomerization of 1,5-hexadiene, 2-methyl-1,5-hexadiene, and 2,5-dimethyl-1,5-hexadiene in presence of calcium amide are very close in value.
2. The results confirm the proposed mechanism of the displacement of double bonds in presence of metal amides.

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*Original Russian pagination. See C.B. Translation.

ORGANOLITHIUM COMPOUNDS IN THE SYNTHESIS OF ALKYL- AND ARYL-PHOSPHONOUS ESTERS

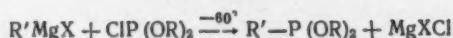
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Translated from *Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk* 1960,
No. 1, pp. 133-134, January 1960

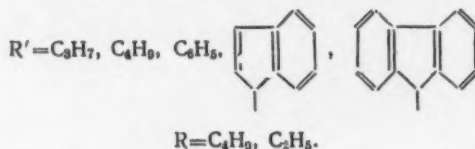
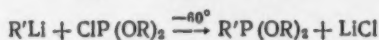
Original article submitted June 15, 1959

We have previously developed a method of synthesizing alkyl- and aryl-phosphonous esters by the replacement of the chlorine atoms of dialkyl phosphorochloridites by alkyl or aryl groups under the action of organo-magnesium compounds. When the reaction is carried out at low temperature, the alkoxy groups scarcely react with organomagnesium compounds and there is selective replacement of the chlorine of dialkyl phosphorochlorides:



It was of interest to determine the possibility of similar selective replacement when more reactive organo-metallic compounds are used, e.g. organolithium compounds, which in some cases have advantages over organo-magnesium compounds for preparative purposes.

In the present investigation it was shown that, in the reaction of organolithium compounds with dialkyl phosphorochloridites at -60° , selective replacement of the chlorine by the organic group of the organometallic compound again occurred with formation of alkyl- and aryl-phosphonous esters:



In some cases the yield of ester was considerably higher than that attained by the use of the organo-magnesium compound. Thus, in the reaction of 9-fluorenylmagnesium bromide [2] with diethyl phosphorochloridite a mixture was formed which consisted mainly of fluorene and a very small amount of diethyl 9-fluorenylphosphonite, which could not be isolated in the pure state. 9-Fluorenyllithium and diethyl phosphorochloridite give this ester in 78% yield. The use of 1-indenyllithium instead of the corresponding organomagnesium compound raises the yield of diethyl 1-indenylphosphonite by about 25%. A higher yield is obtained also when butyllithium is used in the synthesis of dibutyl butylphosphonite.

EXPERIMENTAL

All operations were carried out in an atmosphere of purified nitrogen.

Dibutyl Propylphosphonite. A solution of propyllithium [3], prepared from 35 g of propyl bromide and 5 g of lithium in 150 ml of ether, was filtered and added dropwise to 42.5 g of dibutyl phosphorochloridite in 100 ml

of ether with vigorous stirring; the temperature of the reaction mixture was $-60 \pm 5^\circ$. Ether was then removed under reduced pressure, and 200 ml of petroleum ether was added to the residue; the solution was decanted, the residue was washed with 3-4 50-ml portions of petroleum ether, solvent was removed, and the residue was vacuum distilled. The yield of dibutyl propylphosphonite was 26.4 g (60%); b.p. $59-60^\circ$ (1 mm); n_D^{20} 1.4375; d_4^{20} 0.8836; found MR 65.37; calculated MR 65.12. The literature [1] gives: b.p. $59.8-60.3^\circ$ (1 mm); n_D^{20} 1.4393; d_4^{20} 0.8851.

Dibutyl Butylphosphonite. This was prepared similarly by the action of butyllithium [3] (18.5 g of butyl bromide, 2.3 g of lithium, and 100 ml of ether) on 21.2 g of dibutyl phosphorochloridite in 50 ml of ether. Yield 19 g (81%); b.p. $70.5-71.5^\circ$ (1.5 mm); n_D^{20} 1.4421; d_4^{20} 0.8814; found MR 70.36; calculated MR 69.74. The literature [1] gives: b.p. $68-69^\circ$ (1 mm); n_D^{20} 1.4420; d_4^{20} 0.8839.

Diethyl Phenylphosphonite. This was synthesized from 15.6 g of diethyl phosphorochloridite in 50 ml of ether and a solution of phenyllithium [4] (19.6 g of bromobenzene, 2.1 g of lithium, and 50 ml of ether). Yield 11.2 g (56.5%); b.p. $63-65^\circ$ (1 mm); n_D^{20} 1.5113; d_4^{20} 1.0235; found MR 58.03; calculated MR 56.91. The literature [1] gives: b.p. $62.5-63^\circ$ (1 mm); n_D^{20} 1.5131; d_4^{20} 1.0252.

Diethyl 1-Indenylphosphonite. This was prepared by the action of 1-indenyllithium [5] (36 g of indene, 58 g of butyl bromide, 7 g of lithium, and 250 ml of ether) on 39 g of diethyl phosphorochloridite in 100 ml of ether. Yield 38 g (64.5%); b.p. $99-99.5^\circ$ (1.5 mm); n_D^{20} 1.5491; d_4^{20} 1.0655; found MR 70.55, calculated MR 68.09. Found: C 66.2; 66.2; H 7.5; 7.4; P 13.2; 13.3%. $C_{13}H_{11}PO_2$. Calculated: C 66.1, H 7.2; P 13.1%.

When 1-indenylmagnesium bromide was used [6], the yield of diethyl 1-indenylphosphonite was 40%.

Diethyl 9-Fluorenylphosphonite. A solution of 9-fluorenyllithium [7] (prepared by gradual addition of 20.8 g of fluorene in 100 ml of tetrahydrofuran* over a period of three hours to 5.2 g of chopped lithium wire in 100 ml of tetrahydrofuran, after which the mixture was allowed to stand for 50 minutes at 20°) was treated with 15.6 g of diethyl phosphorochloridite in 50 ml of tetrahydrofuran; the yield of diethyl 9-fluorenylphosphonite was 22.3 g (78%); b.p. $148.5-149^\circ$ (2 mm); m.p. $67.5-70^\circ$ (sublimed at 2 mm). Found: C 71.0; 71.0; H 6.7; 6.5; P 10.8; 10.8%. $C_{17}H_{13}PO_2$. Calculated: C 71.3; H 6.7; P 10.8%.

SUMMARY

1. Organolithium compounds can be applied for the synthesis of alkyl- and aryl-phosphonous esters by the method developed earlier for organomagnesium compounds.
2. In some cases organolithium compounds give better yields of phosphonous esters than the corresponding organomagnesium compounds.

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* The tetrahydrofuran was purified by prolonged boiling over sodium and subsequent distillation.

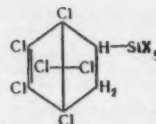
** Original Russian pagination. See C. B. Translation.

SYNTHESIS OF ORGANOSILICON MONOMERS
FROM HEXACHLOROCYCLOPENTADIENE
AND TETRACHLORO-5,5-DIFLUOROCYCLOPENTADIENE

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Translated from *Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk* **1960**,
No. 1, pp. 135-138, January 1960
Original article submitted June 15, 1959

Little information is available on organosilicon monomers of the type



, in which X is,

e.g., an organic radical, halogen, or an OR group. The data which have appeared recently are presented mainly in the form of brief communications in patents [1-5]. It is stated that such monomers can be used for the preparation of silicone greases and oils having various interesting properties [4, 5].

TABLE 1










No.	Group	Group re- fraction found from exptl. data	Group refrac- tion calculated from bond re- fractions
1		58.65	59.66
2		49.03	50.04

In this connection it was of interest to prepare some new monomers of this class with the aid of the Diels-Alder reaction. In this reaction we used not only hexachlorocyclopentadiene, but also tetrachloro-5,5-difluorocyclopentadiene. In both cases the reaction went fairly readily. However, as Table 2 shows, tetrachloro-5,5-difluorocyclopentadiene reacted more readily, particularly when there was a hydrogen attached to the silicon of the dienophile. In the last case the reaction was particularly rapid. It is known that this peculiarity of tetrachloro-5,5-difluorocyclopentadiene is shown also in reactions with organic dienophiles [6]. However, not all the organosilicon dienophiles reacted so readily with hexachlorocyclopentadiene and tetrachloro-5,5-difluorocyclopentadiene; $\text{CH}_2 = \text{CHClSiCl}_3$, $\text{ClCH} = \text{CHSiCl}_3$, and $\text{C}_2\text{H}_5\text{Si}(\text{Cl})_2$; $\text{CF} = \text{CF}_2$ did not undergo diene condensation under our conditions. In these cases the original

compounds were isolated in the fractionation of the reaction products, and only in the case of trichloro (1-chlorovinyl) silane was a very small amount of a wide fraction of addition products obtained.

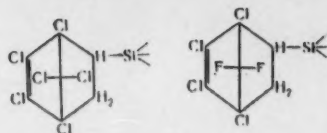
All the above-noted peculiarities of the diene condensation of the two cyclopentadiene derivatives with organosilicon dienophiles may be explained by the superposition of two effects, steric and inductive; this concerns both the diene and the dienophile. Note should be taken also of the quite definite discrepancies between

TABLE 2

Expt.	Reactants		Reaction temp (°C)	Reaction time (hr)	Wt. of reaction products (g)	Yield of diene condensation product	
	diene	dienophile				(g)	(%)
1		CH ₂ =CHSiCl ₃	190	6,5	83,7	42,7	49,0
2		CH ₂ =CHSiCl ₃	130-150	5,3	5,9	3,3	56,0
3		CH ₂ =CHSiCl ₃	138-190	3,25	79,4	59,8	72,4
4		CH ₂ =CHSiCl ₃	105-150	8	4,1	—	—
5		CH ₂ =CH-SiCl ₂ -C ₆ H ₅	146,5-202	4,2	6,0	3,2	50,0
6		• CH ₂ =CHSiCl ₂ -H	137-194	1,6	12,2	—	—
7		CH ₂ =CH-CH ₂ -SiCl ₂ -H	123-134	3,75	8,8	4,3	41,7
8		CH ₂ =CH-CH ₂ -SiCl ₂ -H	128-250	1,8	7,8	4,2	48,8
9		• CH ₂ =CHSiCl ₂ -H	72-152	0,8	4,7	2,9	56,8

* These compounds were prepared by G. V. Odabashyan.

the found and calculated molecular refractions for all the compounds obtained (Table 3); the calculated molecular refraction exceeds the value found by 0.76–1.81 units. By the use of the experimental values of the molecular refractions of these compounds, more exact values can be found of the group refractions for the bonds (Table 1).



EXPERIMENTAL

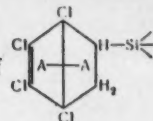
Tetrachloro-5,5-difluorocyclopentadiene was prepared in three stages under the conditions described in the literature [7, 8]; b.p. 70° (25 mm); d_4^{20} 1.6425; n_D^{20} 1.4925. Hexachloropentadiene was prepared for the reaction by distillation of the commercial product; b.p. 104° (9 mm); d_4^{20} 1.7135; n_D^{20} 1.5635.

The diene condensation was carried out by refluxing the reactants together in a flask. The conditions and results of the experiments are presented in Table 2. The physical properties of the products are presented in Table 3.

SUMMARY

1. The preparation was carried out of new organosilicon monomers of the type $RSiX_3$ (X is alkyl, halogen,

or hydrogen) in which the group R attached to silicon is the bicyclic group of



, in which A is

Cl or F.

2. Tetrachloro-5,5-difluorocyclopentadiene undergoes the Diels-Alder reaction with vinyl- and allyl-chlorosilanes more readily than hexachlorocyclopentadiene does, particularly when there is a hydrogen attached to silicon.

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STEPWISE SYNTHESIS OF POLY (ISOPROPYL VINYL ETHER)

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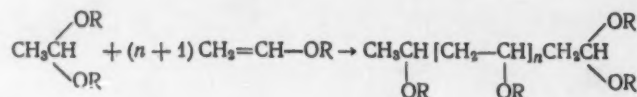
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Translated from *Izvestiya Akademii Nauk SSSR, Otdelenie*

Khimicheskikh Nauk, No. 1, pp. 138-139, January 1960

Original article submitted June 19, 1959

The stepwise nature of the ionic polymerization of alkyl vinyl ethers is of particular interest in that it permits the preparation of the simplest polymerization products, i.e., the dimers, trimers, etc. The behavior of individual compounds such as these provides the most precise basis for determining the laws relating structure, composition, viscosity, and molecular weight. We have already described the stepwise polymerization of ethyl vinyl and butyl vinyl ethers [1,2]. In the present paper we describe the stepwise polymerization of isopropyl vinyl ether, a reaction which proceeds in accordance with the following scheme:



in which $n = 0, 1, 2, 3$, etc.

EXPERIMENTAL

Synthesis of 1,1,3-Triisopropoxybutane. The reaction was carried out in a three-necked flask fitted with mercury-sealed stirrer and reflux condenser. Isopropyl vinyl ether (43 g, 0.5 mole) b.p. 55-56°; n_D^{20} 1.3840; d_4^{20} 0.7520, was added dropwise to a stirred mixture of acetaldehyde diisopropyl acetal (146 g, 1 mole) b.p. 126-128°; n_D^{20} 1.3890; d_4^{20} 0.8142 and catalyst (2 g of a 5% solution of FeCl_3 in butyl alcohol), which was warmed to 45°. The rate of addition of the ether was controlled so as to keep the temperature in the range 45-50°. After the addition of the ether the reaction was allowed to continue for 1-1.5 hours. The catalyst was precipitated with anhydrous sodium carbonate powder (3 g) (stirring for three hours), and the precipitate was filtered off. The filtrate was vacuum distilled. After repeated distillation we isolated 1,1,3-triisopropoxybutane in 25% yield (47 g); b.p. 77.5-78° (4 mm); d_4^{20} 0.8600; n_D^{20} 1.4120; mol.wt. 230; found MR 67.27; calculated for $\text{C}_{15}\text{H}_{28}\text{O}_3$ MR 67.163. Found: C 66.75; 66.56; H 12.01; 12.01%. $\text{C}_{15}\text{H}_{28}\text{O}_3$. Calculated: C 67.19; H 12.14%.

Synthesis of 1,1,3,5-Tetraisopropoxyhexane. The reactants were 81.4 g (0.352 mole) of 1,1,3-triisopropoxybutane and 15.1 g (0.183 mole) of isopropyl vinyl ether. The procedure was analogous to that for the preparation of 1,1,3-triisopropoxybutane. 1,1,3,5-Tetraisopropoxyhexane, obtained in 15% yield (14.5 g), had b.p. 115° (2 mm); n_D^{20} 1.4220; d_4^{20} 0.8787; mol.wt. 318; found MR 91.896; calculated for $\text{C}_{18}\text{H}_{38}\text{O}_4$ MR 92.09. Found: C 66.42; 66.57; H 11.71; 11.71%. $\text{C}_{18}\text{H}_{38}\text{O}_4$. Calculated: C 67.6; H 12%.

Synthesis of 1,1,3,5,7-Pentaisopropoxyoctane. Reaction was between 19 g (0.061 mole) of 1,1,3,5-tetraisopropoxyhexane and 2.58 g (0.031 mole) of isopropyl vinyl ether. The procedure was analogous to that of the first

experiment. 1,1,3,5,7-Pentaisopropoxyoctane, obtained in 12% yield (2.6 g), had b.p. 167–168° (1 mm); n_D^{20} 1.4300; d_4^{20} 0.8940; mol.wt. 404; found MR 116.9; calculated: $C_{23}H_{48}O_5$, MR 116, 629. Found: C 68.09; 68.03; H 11.61; 11.71%. $C_{23}H_{48}O_5$. Calculated: C 68.27; H 11.95%.

Hydrolysis of Isopropoxy Compounds. The isopropoxy compounds obtained were hydrolyzed. The aldehyde liberated was determined by the "hydrolytic oxidation" method [3, 4] using potentiometric titration. The results of the hydrolysis are given in the table.

TABLE

Hydrolysis of Isopropoxy Compounds

	0.4136 N NaOH required (ml)	Amount of isopropoxy cpd. taken (g)	Amount of isopropoxy cpd. found (g)	Degree of hydrolysis (%)
1,1,3-Triisopropoxybutane	8.08	0.7460	0.7401	99
	4.36	0.678	0.672	98.7
1,1,3,5-Tetraisopropoxyhexane	4.9	0.598	0.5958	99
	2.89	0.3344	0.33	98.5

SUMMARY

1. 1,1,3-Triisopropoxybutane, 1,1,3,5-tetraisopropoxyhexane, and 1,1,3,5,7-pentaisopropoxyoctane were synthesized and characterized.

2. The hydrolysis of the isopropoxy compounds was carried out.

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* Original Russian pagination. See C.B. Translation.

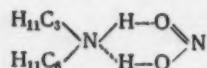
DIPOLE MOMENT OF DICYCLOHEXYLAMINE NITRITE

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Translated from *Izvestiya Akademii Nauk SSSR, Otdelenie
Khimicheskikh Nauk*, No. 1, pp. 139-140, January 1960
Original article submitted June 19, 1959

Dicyclohexylamine nitrite is used as an anticorrosion preparation. It was of interest to determine the polarity of this substance. With this object we measured its dipole moment in benzene solution at 25°. Solutions of the following concentrations (mole fractions) were investigated: 0.000109, 0.000094, and 0.0000809. The dielectric constants of these solutions were found to be 2.2738, 2.2733, and 2.2729. The electron polarization was 65.4 cm³. The values of a , calculated by Hedestrand's method, were 11.17, 10.75, and 10.35. The value of β was 0.8. From these data a value of 4.14 ± 0.04 D was obtained for the dipole moment.

If the compound had been the salt $[(C_6H_{11})_2NH_2]^+[NO_2]^-$, the dipole moment would have been very much greater. The value obtained suggests that this substance occurs in benzene solution as a molecular compound in which the parts are held together by hydrogen bonds, which corresponds to the structure:



The result indicates that, in a nonpolar solvent, an acid and a base may exist not as a salt, but as a molecular compound, as has been found previous in, for example, the work of Sobchik and Syrkin.

We express our thanks to M. N. Polteva for providing the sample for the measurements.

SUMMARY

1. The value of the dipole moment shows that this molecule is not a salt in benzene solution.
2. Dicyclohexylamine and nitrous acid can form a molecular compound containing two hydrogen bonds.

CALCULATION OF THE EFFECT OF IONS ON THE STRUCTURE OF WATER

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Translated from *Izvestiya Akademik Nauk SSSR, Otdelenie
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Original article submitted June 23, 1959

On the basis of Hall's two-structure model of water, Mikhailov and Syrnikov [1] examined the effect of ions on the structure of water. Though the theses developed by the authors of [1] are sensible and interesting from the qualitative point of view, the quantitative relations that they obtained are incorrect.

According to [1]:

$$F_1 - F_1^0 = \bar{U}_1, \quad F_2 - F_2^0 = \bar{U}_2, \quad (1)$$

$$\bar{U}_1 = -n_1 \mu_1 |\bar{E}|, \quad \bar{U}_2 = -n_2 \mu_2 |\bar{E}|, \quad (2)$$

$$n_1 + n_2 = N_1 - hN_2, \quad n_1 = \frac{N_1 - hN_2}{1 + \exp(-\Delta F_1/RT)}, \quad (3)$$

$$F_2' - F_1' = \Delta F_1 = \Delta F_1^0 - N(\mu_2 - \mu_1) |\bar{E}|, \quad (4)$$

$$|\bar{E}| = 2.68 (4\pi/3)^{2/3} \frac{ze}{\epsilon V} N^{2/3} = AN^{2/3}, \quad (5)$$

in which N_1 and N_2 are the numbers of molecules of water and salt in a solution of volume V ; F_1 and F_2 are the free energies of structures 1 and 2 at $N_2 \neq 0$; F_1^0 and F_2^0 are the same quantities when $N_2 = 0$; F_2' and F_1' are the free energies of the structures referred to one mole of water; \bar{U}_2 and \bar{U}_1 are the mean potential energies for the perturbation of the structures due to the ionic field; n_1 and n_2 are the numbers of water molecules in the respective structures; h is the sum of the numbers of water molecules in the hydration envelopes of the cation and anion; N is Avogadro's number; μ_1 and μ_2 are the effective dipole moments of the water molecules in the structures 1 and 2; E is the mean strength of the ionic field; ze is the charge of an ion; ϵ is the dielectric constant.

By the use of the expressions (1)-(5) we can find the relation of the activity coefficient of the electrolyte to concentration. At infinite dilution the free energy of an electrolyte solution is

$$F_0 = F_1^0 + F_2^0 + F_i^0, \quad (6)$$

and at a finite concentration

$$F = F_1 + F_2 + F_i, \quad (7)$$

in which F_i is the free energy of the ions. Hence, taking account of (1) and (2), we obtain:

$$F - F^0 = \Delta F = (F_1 - F_1^0) + (F_2 - F_2^0) + (F_i - F_i^0) = \\ = [n_1(\mu_2 - \mu_1) - (N_1 - hN_2)\mu_2] |\bar{E}| + \Delta F_i. \quad (8)$$

We find the activity coefficient of the electrolyte from the relation

$$kT \ln f_2 = \frac{\partial \Delta F}{\partial N_2} = \\ = \left[(\mu_2 - \mu_1) \frac{\partial n_1}{\partial N_2} + h\mu_2 \right] |\bar{E}| + [n_1(\mu_2 - \mu_1) - (N_1 - hN_2)\mu_2] \frac{\partial |\bar{E}|}{\partial N_2} + \frac{\partial \Delta F_i}{\partial N_2}. \quad (9)$$

Applying (3), (4), and (5), we obtain

$$\frac{\partial n_1}{\partial N_2} = \frac{-h[1 + \exp(-\Delta F_i/RT)] + [(N_1 - hN_2)/RT] \exp(-\Delta F_i/RT) \frac{\partial \Delta F_i}{\partial N_2}}{[1 + \exp(-\Delta F_i/RT)]^2}, \quad (10)$$

$$\frac{\partial |\bar{E}|}{\partial N_2} = \frac{2}{3} AN_2^{-1/3}, \quad (11)$$

$$\frac{\partial \Delta F_i}{\partial N_2} = -N(\mu_2 - \mu_1) \frac{\partial |\bar{E}|}{\partial N_2}. \quad (12)$$

Substituting (10) and (12) in (9), we finally find

$$kT \ln f_2 = \frac{-h(\mu_2 - \mu_1) |\bar{E}|}{[1 + \exp(-\Delta F_i/RT)]} - \\ - \frac{N(N_1 - hN_2)(\mu_2 - \mu_1)^2 \exp(-\Delta F_i/RT)}{RT[1 + \exp(-\Delta F_i/RT)]^2} |\bar{E}| \frac{\partial |\bar{E}|}{\partial N_2} + \\ + h\mu_2 |\bar{E}| + [n_1(\mu_2 - \mu_1) - (N_1 - hN_2)\mu_2] \frac{\partial |\bar{E}|}{\partial N_2} + \frac{\partial \Delta F_i}{\partial N_2}. \quad (13)$$

As $|\bar{E}|(\partial |\bar{E}| / \partial N_2) = 2A^2 N_2^{1/3}/3$, and $\partial \Delta F_i / \partial N_2$ is the Debye term, as $N_2 \rightarrow 0$ the first, second, third, and last terms of Equation (13) tend to zero. The fourth term tends to $-\infty$ because

$$\left(\frac{\partial |\bar{E}|}{\partial N_2} \right)_{N_2 \rightarrow 0} = \infty, \text{ but } [n_1(\mu_2 - \mu_1) - (N_1 - hN_2)\mu_2]_{N_2 \rightarrow 0} = -n_1\mu_1 - n_2\mu_2,$$

from which it follows that when $N_2 \rightarrow 0$, $f_2 \rightarrow 0$, instead of tending to unity. Hence, the method of calculating the effect of the field of ions on the free energy change of water proposed by the authors of [1] leads to an incorrect result. The fact that several assumptions are made in the calculations of [1] does not allow one to establish, without careful analysis, which of them has a determining effect on the final result, but there can be no doubt about the lack of validity of this result.

SUMMARY

The discussion shows the fallaciousness of Mikhailov and Syrnikov's method of calculating the effect of an ionic field on the free energy of water.

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IMPROVED METHOD FOR THE PREPARATION OF DIETHYLALUMINUM HYDRIDE

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Translated from *Izvestiya Akademii Nauk SSSR, Otdelenie
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Original article submitted June 23, 1959

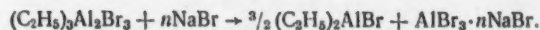
Dialkylaluminum hydrides are of great interest as reducing agents in organic chemistry [1, 2]. Because of their thermal stability they can be used in reactions in which it is difficult to use lithium aluminum hydride. We have shown, for example, that at 120-140° diisobutylaluminum hydride brings about the hydrogenolysis of an ether link [3].

The most important dialkylaluminum hydrides are diethyl- and diisobutyl-aluminum hydrides. Whereas diisobutylaluminum hydride is readily accessible via triisobutylaluminum [1, 4], the laboratory method, described by Ziegler and co-workers [5], for the synthesis of diethylaluminum hydride from diethylaluminum chloride and lithium hydride is very complicated and cumbersome. This method requires the use of a large amount of ether, very fine grinding of the lithium hydride, centrifugation of a reaction mixture that is sensitive to air, careful removal of solid products, and distillation in a high vacuum (10^{-3} – 10^{-4} mm). We propose a simpler method of preparing diethylaluminum hydride from diethylaluminum bromide and lithium hydride, which proceeds in accordance with the equation:



The reaction is carried out with the ether complex of diethylaluminum bromide and, because of the solubility of lithium bromide in ether, fine grinding of the lithium hydride is unnecessary. The reaction starts immediately and proceeds rapidly. Diethylaluminum hydride is separated from lithium bromide and other solid products by dissolution in a hydrocarbon (benzene, hexane). In this case there is no need for centrifugation and distillation in a high vacuum. The yield of diethylaluminum hydride is more than 90% (in [4] it was 70%).

We have developed also a simple method for the preparation of diethylaluminum bromide by the symmetrization of the readily prepared triethyldialuminum tribromide by means of sodium bromide in accordance with the equation:



The process consists in heating the triethyldialuminum tribromide with sodium bromide and vacuum distilling off the diethylaluminum bromide, the yield of which is more than 90%. We have extended this method to the preparation of other dialkylaluminum halides, and this will be the subject of a subsequent communication.

EXPERIMENTAL

Symmetrization of Triethylaluminum Tribromide with Sodium Bromide. A mixture of 52 g (0.14 mole) of triethylaluminum tribromide and 17 g (0.17 mole) of anhydrous sodium bromide was heated with stirring at 200-220° for two hours. Two liquid layers were formed. On cooling, the lower layer solidified. Distillation of the reaction mixture gave 31 g (92%) of diethylaluminum bromide, b.p. 84.2-85° (3mm). Found: C 29.12; 29.36; H 6.14; 6.14; Al 16.54; 16.60; Br 48.30; 48.31%. $C_4H_{10}AlBr$. Calculated: C 29.10 H 6.05; Al 16.30; Br 48.42%.

Preparation of Diethylaluminum Hydride. With stirring, dropwise addition was made of 15.5 ml (0.14 mole) of dry ether to 24 g (0.14 mole) of diethylaluminum bromide. To the resulting ether complex we added 1.45 g (0.18 mole) of finely divided (100 mesh) lithium hydride; the reaction mixture was heated with stirring at 50-60° for one hour. Dry benzene (20 ml) was then added to the mixture. When the precipitate had settled, the clear liquid was carefully siphoned off. This operation was repeated four times. Solvent was distilled off at the water pump. The residue, which was slightly turbid, was heated in a vacuum (1 mm) at 50-60° for 40-60 minutes to remove residual ether; vacuum distillation then gave 11.5 g (92%) of diethylaluminum hydride, b.p. 77° (1 mm). Found: C 55.58; 55.79; H 12.57; 12.53; Al 31.30; 31.05%. $C_4H_{11}Al$. Calculated: C 55.86; H 12.79; Al 31.34%.

Decomposition of diethylaluminum hydride with butyl alcohol gave a mixture of gases consisting of hydrogen and ethane in the proportions 1 : 2.

SUMMARY

A convenient method is proposed for the preparation of diethylaluminum hydride from diethylaluminum bromide and lithium hydride.

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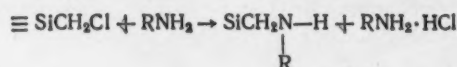
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REACTION OF TETRAALKYL-1,3-BIS- ω -
-CHLOROALKYLDISILOXANES WITH ETHYLAMINE

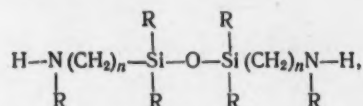
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Translated from *Izvestiya Akademii Nauk SSSR, Otdelenie
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Original article submitted June 27, 1959

The reaction of α -monochloro organosilicon compounds (of the type $\equiv \text{SiCH}_2\text{Cl}$) with primary amines had been studied in several investigations [1-3]. The reaction proceeds in accordance with the scheme:

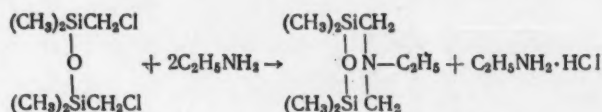


With the object of preparing organosilicon diamines of the type



in which $n = 1$ or 3 , we investigated the reaction between ethylamine and the following dichloro compounds: 1,3-bischloromethyltetramethyldisiloxane and tetraalkyl-1,3-bis-3-chloropropylidisiloxanes.

The first of these dichloro compounds reacted with ethylamine already at room temperature, but the reaction went in an unexpected direction:



with a yield of cyclic monoamine of about 90%. As in reactions of α -monochloro compounds with ethylamine under similar conditions [2] the formation of compounds of the type $\equiv \text{SiCH}_2-\text{N}(\text{R})-\text{CH}_2-\text{Si} \equiv$ was not observed; the only explanation of this course of reaction can be the tendency for the formation of a six-membered ring. In reaction with ethylamine $[\text{ClCH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{CH}_3)(\text{C}_2\text{H}_5)]_2\text{O}$ was found to be much less reactive; there was no reaction in the course of ten days at room temperature. However, under more severe conditions (autoclave, 100°, six hours) reaction went, but in accordance with the usual scheme:

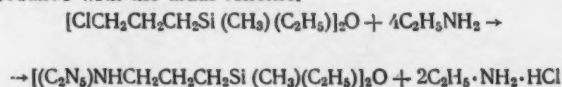


TABLE
Properties of Compounds Obtained

Compound	Formula	Yield (%)	B.p. in °C (p in mm Hg)	n_D^{20}	d_4^{20}	Found MR	Calc. MR	Elementary analysis (%)	
								found	calculated
I*	$[\text{ClCH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{CH}_3)(\text{C}_6\text{H}_5)_2\text{Cl}]$	35	101—103(34)	1,4553	0,8815			Cl 35,6	Cl 35,6
II*	$[\text{ClCH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{C}_6\text{H}_5)_2\text{Cl}]$	44	91—93(10)	1,4600	1,0400			Si 18,1	Si 17,8
III	$[\text{ClCH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{C}_6\text{H}_5)(\text{CH}_3)_2\text{O}]$	70	125(3)	1,4577	0,9950	86,4	86,3	Si 17,0; 16,6 C 48,9; 48,7 H 9,2	Si 16,4 C 48,9 H 9,4
IV	$[\text{ClCH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{C}_6\text{H}_5)_2\text{O}]$	61	165—168(2)	1,4654	1,0062	94,7	95,2		
V	$[\text{H}(\text{C}_2\text{H}_5)_2\text{NCH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{CH}_3)(\text{C}_6\text{H}_5)_2\text{O}]$	69**	152(2)	1,4511	0,8745	102,5	102,5	Si 16,1; 16,5 C 58,2; 58,1 H 12,5; 12,1 N 8,8; 8,7	Si 16,8 C 57,8 H 12,1 N 8,4
VI	$(\text{CH}_3)_2\text{Si}-\text{Si}-\text{CH}_2-\text{N}(\text{C}_6\text{H}_5)_2$ $\quad \quad \quad \quad \quad \quad $ $\quad \quad \quad \text{O} \quad \quad \quad \text{CH}_2$ $\quad \quad \quad \quad \quad \quad $ $\quad \quad \quad \text{N}-\text{C}_6\text{H}_5 \quad \quad \quad \text{CH}_2$ $\quad \quad \quad \quad \quad \quad $ $\quad \quad \quad \text{CH}_2 \quad \quad \quad \text{Si}-\text{CH}_2$ $\quad \quad \quad \quad \quad \quad $ $\quad \quad \quad \text{CH}_3 \quad \quad \quad \text{CH}_2$	91,5**	61(17)	1,4320	0,8768	60,1	59,9	C 46,5; 46,3 H 10,4; 10,5 N 7,7; 8,0	C 47,2 H 10,4 N 7,5
VII	$[\text{H}(\text{C}_2\text{H}_5)_2\text{NCH}_2\text{CH}_2\text{Si}(\text{CH}_3)_2\text{O}]$	58**	123—126(2)	1,4440	0,8658	93,4	93,5	N 9,2; 9,2	N 9,1
VIII	$[\text{HCH}_3\text{NCH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{CH}_3)_2\text{O}]$	53**	112—114(2)	1,4433	0,8733	84,0	84,2	N 9,9; 10,0	N 11,1

• For data in literature see [4].

●●●Calculated on amount of dichloro compound taken.

with a yield of diamine of about 70%. Analogous diamines were obtained from $[\text{ClCH}_2\text{CH}_2\text{H}_2\text{Si}(\text{CH}_3)_2]_2\text{O}$ with $\text{H}_2\text{NC}_2\text{H}_5$ and H_2NCH_3 , also in an autoclave at 100°.

The lower activity of the (3-chloropropyl) silyl compounds, as compared with the (chloromethyl) silyl compound, is most probably to be explained by the nucleophilic character of the replacement of chlorine by an NHR group. It has previously been noted in other cases [5, 6] that γ -chloro organosilicon compounds are much less active than α -chloro compounds in nucleophilic substitution reactions (SN_2).

EXPERIMENTAL

The original $[(\text{ClCH}_2)\text{Si}(\text{CH}_3)_2]_2\text{O}$ was prepared by the hydrolysis of $\text{ClCH}_2(\text{CH}_3)_2\text{SiCl}$. The tetraalkyl-1,3-bis-3-chloropropylidisiloxanes [(III) and (IV), Table 1] are also quite accessible and may be prepared by the addition of allyl chloride to dialkylchlorosilanes at atmospheric pressure in presence of H_2PtCl_6 with subsequent hydrolysis of the dichloro compounds (I) and (II). The properties of the compounds obtained are presented in the table.

Reaction of $\text{C}_2\text{H}_5\text{NH}_2$ with $[(\text{ClCH}_2)\text{Si}(\text{CH}_3)_2]_2\text{O}$. A mixture of 24.7 g (0.107 mole) of 1,3-bis(chloromethyl)-tetramethyldisiloxane and 41.0 g (0.91 mole) of ethylamine was prepared in a thick-walled flask having a firmly fixed ground stopper. After several hours two layers of liquid formed in the reaction mixture: The upper was clear and mobile, and the lower was turbid and thick. The whole contents of the flask were allowed to stand for three days at $20 \pm 5^\circ$, and the upper layer (24.5 g) was then separated and fractionated; 19.9 g of (VI) was obtained. Titration of 0.3634 g of the substance in alcoholic solution with 0.1 N HCl required 17.4 ml 0.1 N HCl. For $\text{C}_8\text{H}_{21}\text{Si}_2\text{NO}$ (VI) the calculated amount is 17.8 ml.

Reaction of $\text{C}_2\text{H}_5\text{NH}_2$ with $[\text{ClCH}_2\text{CH}_2\text{Si}(\text{CH}_3)(\text{C}_2\text{H}_5)]_2\text{O}$. A mixture of 20 g (0.063 mole) of 1,3-bis-3-chloropropyl-1,3-diethyldimethyldisiloxane and 45 g (1 mole) of ethylamine remained as a homogeneous clear mobile liquid when left for ten days under the conditions of the preceding experiment. Repetition of the experiment on the same scale but under autoclave conditions (100°, 6 hours) led to the formation of a nonhomogeneous mixture: a light colorless liquid and a heavy gray slurry. Fractionation of the liquid part of the mixture gave 14.5 g of (V), b.p. 148–152° (2 mm). Titration of 0.1503 g of this substance with 0.1 N HCl required 8.7 ml; the calculated amount for (V) is 9.0 ml. Under analogous conditions, from $[\text{ClCH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{CH}_3)_2]_2\text{O}$, reacting with $\text{H}_2\text{NC}_2\text{H}_5$ and with H_2NCH_3 , we obtained the diamines (VII) and (VIII).

SUMMARY

1. Reaction between 1,3-bis(chloromethyl)tetramethyldisiloxane and ethylamine proceeds at room temperature with formation of the cyclic monoamine 4-ethyl-2,2,6,6-tetramethyl-1-oxa-4-aza-2,6-disilacyclohexane.
2. Tetraalkyl-1,3-bis-3-chloropropylidisiloxanes do not react with ethylamine at room temperature, but at elevated temperatures reaction occurs with formation of a linear diamine.

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* This α, ω -dichloro compound has been prepared by reaction between $\text{ClCH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{CH}_3)\text{Cl}_2$ and CH_3MgCl , with subsequent hydrolysis of the reaction mixture, in accordance with the procedure used previously for the synthesis of tetraalkyl-1,3-biscyanoalkyldisiloxanes [7].

** Original Russian pagination. See C. B. Translation.

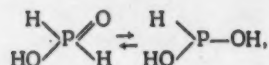
LETTERS TO THE EDITOR

HYOPHOSPHOROUS (PHOSPHINIC) ESTERS

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Translated from *Izvestiya Akademii Nauk SSSR, Otdelenie
Khimicheskikh Nauk*, No. 1, p. 146, January 1960
Original article submitted October 15, 1959

Esters of hypophosphorous acid have not been prepared, and the possibility of their existence has been in doubt: hypophosphorous acid has often been regarded as an acid with a complex anion, $\left[\begin{array}{c} \text{H} \\ \diagup \\ \text{P} \\ \diagdown \\ \text{H} \end{array} \begin{array}{c} \text{O}^- \\ \diagup \\ \text{O} \end{array} \right] \text{H}^+$, these are known not to form esters. On the other hand, A. I. Brodskii and co-workers have proved the presence of tautomerism:



and on this view it is possible for esters to exist.

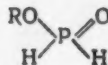
We found that hypophosphorous acid reacts smoothly in the cold with diazoalkanes with formation of the corresponding esters and that, even when the diazoalkane is in great excess, only one molecular proportion of it reacts. We obtained:

$(\text{CH}_3\text{O})\text{P}(\text{O})\text{H}_2$: b.p. 25–25.5° (2.5 mm); n_D^{20} 1.4275; d_4^{20} 1.2177. Found: C 15.3; 15.4; H 6.6; 6.4; P 38.4; 38.5%; MR 16.91 (whence $\text{AR}_P = 5.14$). Calculated: C 15.0; H 6.3; P 38.7%.

$(\text{C}_2\text{H}_5\text{O})\text{P}(\text{O})\text{H}_2$: b.p. 31–32° (2 mm); n_D^{20} 1.4250; d_4^{20} 1.1120. Found: P 32.7; 32.6%; MR 21.64 (whence $\text{AR}_P = 5.25$). Calculated: P 32.9%.

Hypophosphorous esters are colorless liquids which readily decompose at room temperature; when cooled, they solidify (m.p. about –20°), and they can be kept satisfactorily at from –60° to –70°; they oxidize in the air, are hydrolyzed by water, and give qualitative reactions for hypophosphorous acid.

Thus, the formation of hypophosphorous esters is evidence in favor of the covalent structure of the acid and against the complex structure. The inability of the esters to react further with diazoalkanes must be associated with a predominance of the form:



SYNTHESIS OF STANNOUS CHLORIDE FROM ITS ELEMENTS

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Translated from *Izvestiya Akademii Nauk SSSR, Otdelenie
Khimicheskikh Nauk* 1960, No. 1, p. 147, January 1960
Original article submitted October 20, 1959

It is known that stannic chloride (SnCl_4) is obtained when gaseous chlorine reacts with tin. Stannous chloride (SnCl_2) has not been prepared directly from its elements. It is usually prepared by dissolving tin in hydrochloric acid, crystallizing the dihydrate out, and dehydrating it. As a result of an investigation of the action of gaseous chlorine and of stannic chloride on tin, we have found conditions for the preparation of stannous chloride by the action of gaseous chlorine on tin. It was shown that the process can be carried out in two different ways: at a temperature above the boiling point of stannous chloride (606°), and at a temperature somewhat above the melting point of tin ($235\text{--}300^\circ$).

An essential condition for the success of the process is the ensuring of adequate contact between the gas phase and the reaction surface of the tin, which must be in excess. This problem was solved in different ways in the high-temperature process (evaporation of SnCl_2 from the surface) and in the low-temperature process (renewal of the tin surface). The proposed methods can be used not only in the laboratory, but also on an industrial scale. Successful trials have been made on an industrial scale. The principles of the low-temperature process, and also the apparatus which we have proposed for use in the process, may be applied in the preparation of various other substances. In particular, we have succeeded in preparing titanium trichloride from the tetrachloride by this method.

GEOMETRIC ISOMERS OF PROPENYL COMPOUNDS OF TER- AND QUINQUE-VALENT ANTIMONY

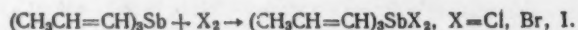
A. N. Nesmeyanov, A. E. Borisov,
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Khimicheskikh Nauk* 1960, No. 1, p. 147, January 1960

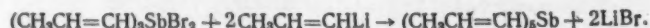
Original article submitted October 29, 1959

In continuation of our study of the stereochemistry of ethylenic organometallic compounds we synthesized a series of geometric isomers of propenyl compounds of ter- and quinque-valent antimony. With antimony trichloride cis- and trans-propenyllithiums gave tri-cis- and tri-trans-propenylantimonies, respectively. Reaction of these isomers with halogens led to a series of isomeric compounds of quinquevalent antimony:

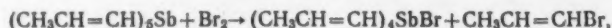


Chlorine- and bromine-containing cis-compounds are crystalline substances, and the trans-compounds are liquids. The assignment of configurations was made on the basis of the infrared absorption spectra and was in accord with the regularities that we have observed [1].

We synthesized the liquid geometric isomers of pentapropenylantimony from the cis- and trans-isomers of tripropenylantimony dibromide and the corresponding isomers of propenyllithium:



They differed in refractive index and infrared absorption spectrum. By treatment of these isomers with a definite amount of bromine we obtained two different forms of tetrapropenylstibonium bromide:



These differed in melting point and infrared absorption spectrum.

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*Original Russian pagination. See C. B. Translation.

REACTION OF FREE RADICALS WITH UNSYMMETRICAL ORGANOMERCURY COMPOUNDS

A. N. Nesmeyanov, A. E. Borisov,
A. I. Kovredov, and E. I. Golubeva

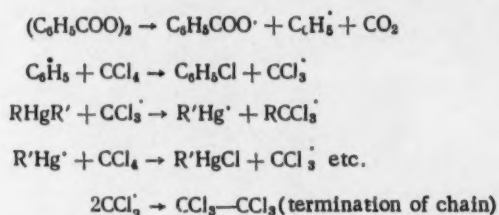
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Translated from *Izvestiya Akademii Nauk SSSR, Otdelenie
Khimicheskikh Nauk* 1960, No. 1, p. 148, January 1960

Original article submitted October 29, 1959

We have described [1] reaction initiated by benzoyl peroxide between carbon tetrachloride and symmetrical organomercury compounds; this proceeds by the equation: $R_2Hg + CCl_4 \rightarrow RHgCl + RCl_3$.

In the present investigation we applied this homolytic-exchange reaction to unsymmetrical dialkyl (or aryl) mercurys. Compounds of formula $RHgR'$ react with carbon tetrachloride in presence of the peroxide in accordance with the scheme:



The radical bound to mercury in $R'HgCl$ is always the less electronegative radical [2], and RCl_3 contains the more electronegative radical. The free radical $CCl_3\cdot$ attacks the same mercury-attached radical that undergoes electrophilic attack by a hydrogen ion in the decomposition of $RHgR'$ with acid. The results are summarized in the table.

TABLE

Original compound	State of product	Reaction products isolated (yield in %)
$C_6H_5HgC_2H_5$	Oil	C_2H_5HgCl (87%) + $C_6H_5CCl_3$
$C_6H_5CH_2HgC_4H_9$	Oil	$C_6H_5CH_2HgCl$ (73%) + $C_4H_9CCl_3$ (58%)
$C_6H_5HgC_6H_5$	Oil	C_6H_5HgCl (76%) + $C_6H_5CCl_3$ (72%)
$C_6H_5HgC_6H_{11}$	Solid, m.p. 59-61°	$C_6H_{11}HgCl$ (83%) + $C_6H_5CCl_3$ (43%)
$C_6H_5HgCH_2C_6H_5$	Oil	$C_6H_5CH_2HgCl$ (73%) + $C_6H_5CCl_3$ (33%)
$C_6H_5HgC_6H_4CH_3-p$	Solid, m.p. 167-192°	C_6H_5HgCl (88%) + $p-CH_3C_6H_4CCl_3$ (82%)
$p-CH_3C_6H_4HgC_6H_4CH_3-o$	Solid, m.p. 159-189°	$o-CH_3C_6H_4HgCl$ (57%) + $o-CH_3C_6H_4CCl_3$ (40%) + + $p-CH_3C_6H_4HgCl$ (43%) + $p-CH_3C_6H_4CCl_3$ (60%)
$C_6H_5HgC_{10}H_7-\alpha$	Solid, m.p. 165-195°	C_6H_5HgCl (73%) + $\alpha-C_{10}H_7CCl_3$ (73%)

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SIGNIFICANCE OF ABBREVIATIONS MOST FREQUENTLY
ENCOUNTERED IN SOVIET PERIODICALS

FIAN	Phys. Inst. Acad. Sci. USSR.
GDI	Water Power Inst.
GITI	State Sci.-Tech. Press
GITTL	State Tech. and Theor. Lit. Press
GONTI	State United Sci.-Tech. Press
Gosenergoizdat	State Power Press
Goskhimizdat	State Chem. Press
GOST	All-Union State Standard
GTTI	State Tech. and Theor. Lit. Press
IL	Foreign Lit. Press
ISN (Izd. Sov. Nauk)	Soviet Science Press
Izd. AN SSSR	Acad. Sci. USSR Press
Izd. MGU	Moscow State Univ. Press
LEIIZhT	Leningrad Power Inst. of Railroad Engineering
LET	Leningrad Elec. Engr. School
LETI	Leningrad Electrotechnical Inst.
LETIIZhT	Leningrad Electrical Engineering Research Inst. of Railroad Engr.
Mashgiz	State Sci.-Tech. Press for Machine Construction Lit.
MEP	Ministry of Electrical Industry
MES	Ministry of Electrical Power Plants
MESEP	Ministry of Electrical Power Plants and the Electrical Industry
MGU	Moscow State Univ.
MKhTI	Moscow Inst. Chem. Tech.
MOPI	Moscow Regional Pedagogical Inst.
MSP	Ministry of Industrial Construction
NII ZVUKSZAPIOI	Scientific Research Inst. of Sound Recording
NIKFI	Sci. Inst. of Modern Motion Picture Photography
ONTI	United Sci.-Tech. Press
OTI	Division of Technical Information
OTN	Div. Tech. Sci.
Stroiizdat	Construction Press
TOE	Association of Power Engineers
TsKTI	Central Research Inst. for Boilers and Turbines
TsNIEL	Central Scientific Research Elec. Engr. Lab.
TsNIEL-MES	Central Scientific Research Elec. Engr. Lab.-Ministry of Electric Power Plants
TsVTI	Central Office of Economic Information
UF	Ural Branch
VIESKh	All-Union Inst. of Rural Elec. Power Stations
VNIIM	All-Union Scientific Research Inst. of Metrology
VNIIZhDT	All-Union Scientific Research Inst. of Railroad Engineering
VTI	All-Union Thermotech. Inst.
VZEI	All-Union Power Correspondence Inst.

Note: Abbreviations not on this list and not explained in the translation have been transliterated, no further information about their significance being available to us. — Publisher.

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